

Light Impurities in Simple Metals: Electronic Structure and Energy Profiles

INAUGURAL-DISSERTATION

zur Erlangung der Philosophischen Doktorwürde
vorgelegt der
Philosophischen Fakultät II
der Universität Zürich

von

STEFAN ESTREICHER
aus Neuchâtel (CH)

1983

Begutachtet von Prof. Dr. P. F. Meier und Prof. Dr. A. Thellung

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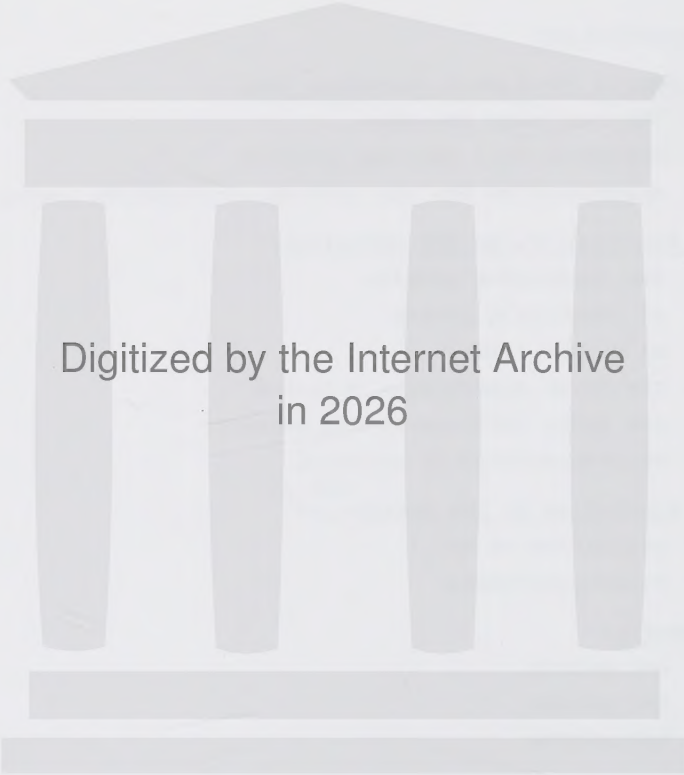
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LIGHT IMPURITIES IN SIMPLE METALS: ELECTRONIC STRUCTURE AND ENERGY PROFILES.

TABLE OF CONTENTS

Abstract	1
<u>I. Introduction</u>	2
<u>II. Density functional formalism (DFF):</u>	
1. The two basic theorems	8
2. Reduction to a one-body problem	11
3. Approximation for the exchange-correlation energy	13
<u>III. Solution to the DFF equations:</u>	
1. The scattering problem	16
a) scattering states	18
b) bound states	21
2. The first approximate solution	22
3. The fully self-consistent density	24
4. Parametrization of $\Delta n(r)$	27
<u>IV. Calculation of the energy:</u>	
1. Evaluation of $E(\vec{R}_\mu)$	32
2. Pseudopotentials	35
<u>V. Results:</u>	
1. bcc metals	40
2. fcc metals	45
3. hcp metals	51
<u>VI. Qualitative study of other effects:</u>	
1. Lattice relaxation in Al and Cs	54
2. Effect of substitutional impurities in Al	58
<u>VII. Summary and conclusions</u>	62
<u>Appendices:</u>	
A. Riccati-Bessel functions	64



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B. Numerov method	65
C. Asymptotic behavior of the density	67
D. Evaluation of the energy for a single ion	70
References	72
Acknowledgments	76
Lebenslauf	77

Abstract

The self-consistent density-functional formalism has been used to calculate electronic densities around light impurities in jellium. The resulting charge densities have been fitted to a simple analytic function of the jellium parameter r_s for all metallic densities. Energy differences for muons and protons have then been calculated along various directions in 17 simple metals crystallizing in the bcc, fcc and hcp structures, using up to 6 different local pseudopotentials in first order perturbation theory. The dependence of the energy on the choice of pseudopotential is discussed. In most metals, it is possible to predict either the stable interstitial site or the most probable diffusion paths, and to give an estimate of the height of diffusion barriers. The zero-point energy of muons and protons in the calculated potentials has been estimated and the problem of localization discussed. The effect of the zero-point motion of the lattice ions is shown to be negligible. The modification of the energy profiles with lattice relaxation has been studied in Al and Cs. It is shown, in the case of Al, that substitutional impurities can attract or repel protons and muons. In a number of cases, a muon could even be trapped in the neighborhood of the substitutional impurity.

I. INTRODUCTION

The study of imperfect crystalline solids has been a topic of great interest to physicists, chemists, metallurgist and material scientists for many years. This interest stems not only from the fact that no solid in nature exists in a 100% pure state but also because defects greatly influence mechanical, thermodynamical and electronic properties of crystals.

There is a large variety of different imperfections in solids: point defects (interstitial or substitutional impurities and their clusters, vacancies,...), dislocations, boundaries, stacking faults, surfaces,... . The study of defects in solids covers therefore an enormous area of research.

In the present work, we shall be concerned with the discussion of the electronic structure and energetics of one kind of point defects in simple metals: the hydrogen-like interstitials. The interest in the study of the behavior of hydrogen in metals is due as well to its technological importance in metallurgy and in hydrogen storage materials as to the basic solid state physics problems involved.

Metallic hosts are characterized by a lattice of positive ions in a sea of itinerant conduction electrons which screen the ions within a short distance, the Wigner-Seitz radius. The so-called "simple metals" include all metals with small ion cores and no d- or f- like electrons close to the Fermi level (noble metals are often also treated as simple metals, as well as Cd and Zn). In the case of transition metals with d- bands crossing the Fermi level, the d- character of the electrons as well as the local geometry are important factors in the hydrogen-metal interaction (tendency to form hydrides).

The implantation of a charged impurity in such a system leads to the loss of periodicity of the lattice and to a redistribution of the conduction electrons. One is therefore faced with the

problem of making a suitable choice for the electron-impurity potential. When the impurity possesses some core-electrons, the potential experienced by a conduction electron due to the implanted ion may be simplified by realizing that the orthogonalization of the conduction electron wave functions to the impurity core orbitals leads to a weak potential. Therefore, simple theories based on statistical models^{1,2,3}, on the Hartree model⁴ or on perturbation theory⁵ are justified. However, when hydrogen is implanted into a metal, it dissociates into a proton and an electron. This gives rise to a strong electron-impurity potential, the bare Coulomb potential, which is divergent at the proton site and can therefore never be treated as a weak perturbation: nonlinear theories are necessary to study the electronic structure of protons in metals.

In addition to the proton, the behavior of particles carrying a unit positive charge is also relevant to the positive muon⁶ (μ^+) and pion⁷ (π^+) which, in recent years, have been used as probes in solids. Their use has added a new dimension to the otherwise conventional methods of studying hydrogen in solids.

As concerns the interaction with the ions and electrons in simple metals, muons and pions behave identically to the proton and its heavier isotopes deuterium and tritium. However, the large mass difference ($m_p \sim 6.7 m_\pi \approx 8.9 m_\mu$) implies very different diffusion properties: the excitation energies for thermally activated diffusion and the tunnelling matrix elements (which determine the band-like diffusion possible at low temperatures) strongly depend on the particle mass. Further, the amplitude of the zero-point motion and the zero-point energy change considerably from one particle to the other. This provides a unique opportunity to study isotope effects by varying the mass of the point charge by as much as a factor 27 from muon to tritium.

Various approaches have been developed to deal with these light

impurities: first-principle calculations like Hartree-Fock and molecular orbital methods⁸, or molecular cluster and band structure calculations⁹ have been used to investigate particular aspects of electronic structure at point defects in metals. Some 20 years ago, a powerful theory of inhomogeneous electron systems in their ground state has been developed by Hohenberg, Kohn and Sham¹⁰⁻¹². In their theory, known as the Density Functional Formalism (DFF)¹³, the central quantity is the electron density, the basic role of which is established by a theorem demonstrating that the properties of the system (in particular the ground-state energy) are functionals of this density. The theory is only restricted by an incomplete knowledge of the exchange-correlation energy in systems of interacting electrons. The DFF as well as the problem of exchange-correlation are discussed in Sec. II.

The DFF has been extensively used in impurity problems via two different approaches which simplify the interaction with the lattice ions by introducing pseudopotentials.

In the spherical solid model¹⁴, the electron density is calculated self-consistently in the spherically averaged potential consisting of the bare Coulomb potential of the impurity and of the ion pseudopotentials. This method has been used successfully to explain Knight shifts at interstitial muons in almost all simple metals¹⁵. The spherical solid model seems to be well justified to describe properties at highly symmetric interstitial sites. For less symmetric positions of the impurity, the non-spherical corrections, calculated by Perrot and Rasolt¹⁶, are small.

Another approach (first proposed by Lang and Kohn¹⁷ for studying surfaces) includes pseudopotentials in first order perturbation theory, but takes fully into account the anisotropy of the lattice. The present work is based on this second model, which was first used for impurity problems by Popovic and Stott^{18,19}. The periodic arrangement of positive lattice ions is

first neglected and replaced by a uniform positive background of density $n_0 = Z_I/\Omega$, where Z_I is the valence of the ions and Ω the atomic volume. This approximation is known as the jellium model. The wave functions of the unperturbed electrons are plane waves and the various metals are represented by a conventional parameter r_s given by

$$\frac{4\pi}{3} r_s^3 = n_0^{-1} . \quad (I.1)$$

Thus, r_s represents the radius of a sphere occupied by one electron in the homogeneous electron gas. For metallic densities, its value varies from 1.86 (Be) up to 5.63 (Cs) (a.u.). The implantation of a point unit charge is equivalent to an external charge perturbation $n_{\text{ext}}(\vec{r})$ given by

$$n_{\text{ext}}(\vec{r}) = \delta(\vec{r}) + n_0 \Theta(\vec{r}-\vec{R}) , \quad (I.2)$$

where R is the radius of the cavity containing the impurity. In the case of a proton trapped at the center of a mono-vacancy, R is equal to R_{ws} (Wigner-Seitz radius), and for an interstitial impurity R is 0.

The calculation of the perturbed charge density $\Delta n(\vec{r}) = n(\vec{r}) - n_0$ around the impurity, performed within the DFF, is described in Sec.III, which also contains a parametric formula, depending only on r_s and r , that simplifies to a large extent all calculations starting with impurities in jellium.

Finally, the positive background is replaced by a pseudopotential at each lattice site. In first order perturbation theory, the energy of a point charge with valence $Z = 1$, located at $\vec{R}_\mu$, is given by the simple expression

$$E(\vec{R}_\mu) = \sum_{\vec{\ell}} \left\{ \frac{Z}{|\vec{R}_\mu - \vec{R}_{\vec{\ell}}|} + \int d\vec{r} \Delta n(\vec{r} - \vec{R}_\mu) W(\vec{r} - \vec{R}_{\vec{\ell}}) \right\} + E_0 , \quad (I.3)$$

where Z stands for the valence of the host ions. E_0 contains all terms independent of the position of the impurity, which therefore do not contribute to energy differences. In the

following, E_0 is 0. $W(\vec{r})$ is the difference between the local unscreened pseudopotential and the potential induced by the positive background charge of the jellium. In the present work, since we are not interested by the total heat of solution but only by energy differences at various sites, we drop this constant term. The evaluation of Eq. I.3 and the forms of the various pseudopotentials that can be found in the literature are discussed in Sec. IV. The proton and the muon are treated as infinitely heavy particles, except when discussing isotope effects via the zero-point energy of the impurity.

A number of calculations, using the spherical solid model or based on the jellium model, have been carried out with varying degree of sophistication. Although the results agree reasonably well for a proton in an electron gas, no clear consensus has been reached regarding the energetics including the lattice ions. As an example, in the case of Al, the results^{19,20,21} differ not only by the numerical values of the barrier heights, but also by the interstitial site of minimum energy. These discrepancies are partially due to the approach used and to differently calculated electronic densities, but the main reason lies in the choice of the pseudopotential.

The present work gives a systematic attempt to cope with these problems. In order to gain insight into the accuracy of the use of pseudopotentials, we have calculated the energy profiles in 17 simple metals using up to six different local pseudopotentials proposed in the literature. As expected, the results depend on the choice of the pseudopotential. However, in many cases, it is possible to make reliable statements about the possibility of localization of muons and protons, and to estimate the heights of diffusion barriers. In a few cases, however, different pseudopotentials lead to quite different energy profiles. These results are discussed in Sec. V for the bcc, fcc and hcp metals investigated.

In Sec.VI, two effects are qualitatively investigated: first, we studied the influence on the energy profiles of lattice relaxation of the first and second neighboring shells around the impurity, in the cases of a fcc metal with high electronic density (Al) and of a bcc metal with low density (Cs). Then, we discuss the effect of a substitutional impurity on the behavior of a muon in Al: it can be seen that a substitutional impurity attracts or repels the muon, depending on its core radius and valence. In some cases, the attraction is strong enough to trap the muon in the vicinity of the substitutional impurity, as observed experimentally.

The main results are summarized in Sec.VII.

Except when explicitly mentioned, all quantities are in atomic units ($\hbar = m_e = e = 1$).

II. DENSITY FUNCTIONAL FORMALISM (DFF)

In a series of three papers¹⁰⁻¹², Hohenberg, Kohn and Sham (HKS) have laid the foundations of a theory of inhomogeneous interacting electron systems. The theory represents a systematic extension of the Thomas-Fermi ideas and is capable (in principle) of providing exact answers. HKS developed a formal variational principle for the ground-state energy in which the density $n(\vec{r})$ is the variable function. The central result of the theory is the existence of a one-particle effective potential, and the full N-body problem is reduced to solving one-particle Schrödinger equations leading to the exact ground-state electron density. The wave functions appearing in the resulting one-particle Schrödinger equation can be interpreted²² in terms of pseudo-particles having zero net charge (this interpretation is based on an exact expression of the N-body exchange-correlation energy in terms of pair-correlation functions). Therefore, the single-particle wave functions, obtained from the one-particle effective potential via the Schrödinger equation, have no direct interpretation in terms of electron wave functions, and the relevant quantity of the theory is the charge density.

1. The two basic theorems

HKS consider a system of electrons in its ground state, assumed for simplicity to be non-degenerate, under the influence of an external potential $v(\vec{r})$. The second-quantized Hamilton operator H consists of the kinetic energy T , the electron-electron Coulomb interaction U and the external potential V :

$$H = T + U + V \quad (\text{II.1})$$

where

$$T = - \frac{1}{2} \int d\vec{r} \, \vec{\nabla} \Phi^\dagger(\vec{r}) \cdot \vec{\nabla} \Phi(\vec{r}) \quad , \quad (\text{II.2})$$

$$U = \frac{1}{2} \int d\vec{r} \, d\vec{r}' \, \frac{\Phi^\dagger(\vec{r}) \Phi^\dagger(\vec{r}') \Phi(\vec{r}') \Phi(\vec{r})}{|\vec{r} - \vec{r}'|} \quad , \quad (\text{II.3})$$

and

$$v = \int d\vec{r} \phi^\dagger(\vec{r}) v(\vec{r}) \phi(\vec{r}) . \quad (\text{II.4})$$

The ground state is denoted by Ψ , the associated density by $n(\vec{r})$ and the number of particles by $N = \int d\vec{r} n(\vec{r})$.

DFF rests on two theorems given in the first paper¹⁰:

- 1) the ground-state wave function (i.e. all ground state properties) is a unique functional of the density.

(A functional is a quantity which depends on a variable function and not on a number of discrete independent variables).

Proof: ab absurdo: only one $v(\vec{r})$ exists which gives the density $n(\vec{r})$.

We suppose therefore that there exists another external potential $v'(\vec{r})$, with ground state Ψ' , leading to the same density

$$n'(\vec{r}) = n(\vec{r}) . \quad (\text{II.5})$$

If $v'(\vec{r})$ and $v(\vec{r})$ differ by more than a constant, $\Psi \neq \Psi'$ since they obey two different Schrödinger equations. Let H and H' be the Hamiltonians associated with Ψ and Ψ' , and the corresponding ground-state energies be E and E' . By the minimal property of the ground state²³

$$\begin{aligned} E' &= \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H - V + V' | \Psi \rangle \\ &\quad \uparrow \\ &\quad (\text{strict: } \Psi' \neq \lambda \Psi) \\ &= E + \int d\vec{r} n(\vec{r}) \{v'(\vec{r}) - v(\vec{r})\} . \end{aligned} \quad (\text{II.6})$$

The same applies to the non-primed quantities:

$$E < E' + \int d\vec{r} n'(\vec{r}) \{v(\vec{r}) - v'(\vec{r})\} . \quad (\text{II.7})$$

Using the assumption (II.5), the sum of Eqs. II.6 and II.7 leads to the inconsistency

$$E' + E < E + E' . \quad (\text{II.8})$$

Thus, $v(\vec{r})$ is a unique functional of $n(\vec{r})$.

Remarks:

1. One has to be more careful in the case of a degenerate ground state.
2. In the Schrödinger equation one accepts readily that $n(\vec{r})$ and all properties of the system are functionals of $v(\vec{r})$ and can be determined from $v(\vec{r})$ via the Schrödinger equation. The validity of the converse is not so obvious and the theorem was first greeted with a great skepticism, based on the feeling that the properties of a system could be determined by the one-particle density matrix and that the density $n(\vec{r})$ (being only its diagonal part) contained less information. However, the theorem has so far stood the test of time.

ii) for a given external potential, the ground-state energy is minimal for the correct $n(\vec{r})$.

Proof: HKS define a universal functional F , valid for any number of particles and any external potential

$$F\{n\} = \langle \Psi | T + U | \Psi \rangle . \quad (\text{II.9})$$

The energy functional

$$E_v\{n\} = F\{n\} + \int d\vec{r} \ v(\vec{r}) n(\vec{r}) \quad (\text{II.10})$$

is clearly the ground-state energy if $n(\vec{r})$ is the ground-state density. Using the notation of thm 1):

$$E_v\{n\} = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle . \quad (\text{II.11})$$

From

$$\langle \Psi' | H | \Psi' \rangle = F\{n'\} + \int d\vec{r} \ n'(\vec{r}) v(\vec{r}) = E_v\{n'\} \quad (\text{II.12})$$

follows immediately

$$E_v\{n\} < E_v\{n'\} . \quad (\text{II.13})$$

The whole N-body problem has now been reduced to determining the universal functional F .

Remark:

This proof makes implicitly the assumption that an arbitrary density profile $n'(\vec{r})$ can be produced by an external potential $v'(\vec{r})$.

2. Reduction to a one-body problem

The additional condition $N = \int d\vec{r} n(\vec{r}) = \text{const.}$ is included now using a Lagrange multiplier, and

$$\delta \{ E_v \{ n \} - \mu \int d\vec{r} n(\vec{r}) \} = 0. \quad (\text{II.14})$$

The Euler equation then reads

$$\frac{\delta E_v \{ n \}}{\delta n(\vec{r})} = \mu, \quad (\text{II.15})$$

where μ is the chemical potential. Using Eq. II.10, this can be rewritten as

$$\frac{\delta F \{ n \}}{\delta n(\vec{r})} + v(\vec{r}) = \mu. \quad (\text{II.16})$$

In an electronic system, it is convenient to separate from F the electrostatic interaction which is long-ranged

$$F \{ n \} = G \{ n \} + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (\text{II.17})$$

Further, since the external potential $v(\vec{r})$ is often caused by a distribution of positive charges $n_{\text{ext}}(\vec{r})$ (see e.g. Eq. I.2),

$$v(\vec{r}) = - \int d\vec{r}' \frac{n_{\text{ext}}(\vec{r}')}{|\vec{r} - \vec{r}'|}, \quad (\text{II.18})$$

the total energy can be rewritten as

$$E_v \{ n \} = G \{ n \} + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} - \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n_{\text{ext}}(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (\text{II.19})$$

Finally, the Euler equation (II.15) becomes

$$\frac{\delta G\{n\}}{\delta n(\vec{r})} + V_{es}(\vec{r}) = \mu, \quad (II.20)$$

where the electrostatic potential $V_{es}(\vec{r})$ is defined as

$$V_{es}(\vec{r}) = \int d\vec{r}' \frac{n(\vec{r}') - n_{ext}(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (II.21)$$

The functionals E_v , F and G are still unknown. Kohn and Sham consider now a system of non-interacting particles in the single-particle potential V_s , with Hamiltonian $H = T + V_s$, and ground-state energy $E = \langle \psi_s | H | \psi_s \rangle$. If one defines the functional

$$T_s\{n\} = \langle \psi_s | T | \psi_s \rangle, \quad (II.22)$$

the Euler equation is

$$\frac{\delta T_s\{n\}}{\delta n(\vec{r})} + V_s(\vec{r}) = \mu_s. \quad (II.23)$$

Now, although T_s is unknown, the solutions to the problem are known exactly: ψ_s is simply the Slater determinant of one-particle wave functions satisfying the one-particle Schrödinger equation

$$-\frac{1}{2} \nabla^2 \psi_i(\vec{r}) + V_s(\vec{r}) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (II.24)$$

and

$$n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2. \quad (II.25)$$

Thus, the Euler equation (II.23) can be solved exactly by calculating the one-particle wave functions.

This result is essential to the system of interacting particles. If one defines the exchange-correlation energy functional $E_{xc}\{n\}$ by

$$E_{xc}\{n\} = G\{n\} - T_s\{n\}, \quad (II.26)$$

The Euler equation (II.20) becomes

$$\frac{\delta T_s\{n\}}{\delta n(\vec{r})} + V_{es}(\vec{r}) + \frac{\delta E_{xc}\{n\}}{\delta n(\vec{r})} = \mu, \quad (II.27)$$

which is formally identical to Eq. II.23 if one sets

$$v_{\text{eff}}\{n(\vec{r}), \vec{r}\} = v_{\text{es}}(\vec{r}) + \frac{\delta E_{\text{xc}}\{n\}}{\delta n(\vec{r})} . \quad (\text{II.28})$$

Eq. II.27 can now be solved exactly by computing the solutions of the one-particle Schrödinger equation

$$-\frac{1}{2} \nabla^2 \psi_i(\vec{r}) + v_{\text{eff}}(\vec{r}) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (\text{II.29})$$

which leads to the density

$$n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2 . \quad (\text{II.30})$$

This result is exact. However, $E_{\text{xc}}\{n\}$ is unknown and has to be approximated.

Remarks:

1. $T_{\text{S}}\{n\}$ is not the true kinetic energy since it corresponds to a non-interacting system.
2. It would be tempting to generalize the theory to the case of a non-local potential $v(\vec{r}, \vec{r}')$ and use the density matrix $n(\vec{r}, \vec{r}')$ as a basic quantity. However, this works only as far as ground-state properties become functionals of $n(\vec{r}, \vec{r}')$. In addition, the variational principle breaks down since not all functions of two variables are admissible density matrices. Further, the density matrix of an interacting system cannot be written as a finite sum like Eq. II.30, as shown by Löwdin²⁴.
3. By setting $E_{\text{xc}}\{n\} = 0$, one recovers the Hartree approximation.⁴

3. Approximation for the exchange-correlation energy

For an interacting electron gas, we do not know and therefore must approximate the exchange-correlation functional $E_{\text{xc}}\{n\}$. The simplest and particularly intuitive approximation supposes a slowly varying density and starts with the expansion:

$$E_{xc}\{n\} \approx \int d\vec{r} \epsilon_{xc}(n(\vec{r})) n(\vec{r}) + \frac{1}{2} \int d\vec{r} \epsilon_{xc}^{(2)}(n(\vec{r})) |\vec{\nabla} n(\vec{r})|^2 + \\ + \frac{1}{6} \int d\vec{r} \epsilon_{xc}^{(3)}(n(\vec{r})) \vec{\nabla} n(\vec{r}) \cdot \vec{\nabla} (\vec{\nabla}^2 n(\vec{r})) + \dots \quad (II.31)$$

where $\epsilon_{xc}(n(\vec{r}))$, function of $n(\vec{r})$, is the exchange-correlation energy per electron of a homogeneous interacting electron gas of density $n(\vec{r})$. This function itself is known approximately. The Local Density Approximation (LDA), introduced first by Kohn and Sham¹¹ considers only the first term of the expansion (II.31), i.e. assumes that the contribution of exchange and correlation to the total energy can be accumulated additively from each portion of an inhomogeneous system as if it were locally homogeneous. In terms of density, this implies that $n(\vec{r})$ should not vary too much over distances comparable to $r_s(\vec{r})$, defined by

$$\frac{4\pi}{3} r_s^3(\vec{r}) = n^{-1}(\vec{r}) \quad (II.32)$$

In this approximation, the exchange-correlation potential is given by (see Eq.II.28)

$$V_{xc}\{n\} = \frac{\delta E_{xc}\{n\}}{\delta n(\vec{r})} = \frac{\delta}{\delta n(\vec{r})} \int d\vec{r} n(\vec{r}) \epsilon_{xc}(n(\vec{r})) \\ = \epsilon_{xc}(n(\vec{r})) + n(\vec{r}) \left. \frac{d\epsilon_{xc}}{dn} \right|_{n=n(\vec{r})} \quad (II.33)$$

Thus, V_{xc} is the exchange-correlation part of the chemical potential of a homogeneous electron gas of density $n(\vec{r})$ ²⁵.

There exist various parametric forms for ϵ_{xc} ²⁶⁻³¹. In the actual calculations, we used the parametric form of the result of Singwi et al³¹ proposed by Hedin and Lundqvist³². They write V_{xc} in terms of a correlation enhancement factor β :

$$V_{xc}(r_s(r)) = \beta(r_s(r)) \mu_x(r_s(r)) \quad (II.34)$$

where

$$\mu_x(r_s(r)) = -\frac{1}{\alpha r_s(r)} \quad , \quad \alpha^3 = \frac{4\pi}{9} \quad (\text{II.35})$$

and

$$\beta(r_s(r)) = 1 + 0.0225 \alpha r_s(r) \ln\left\{1 + \frac{21}{r_s(r)}\right\} . \quad (\text{II.36})$$

$r_s(r)$ is defined in Eq. II.32 .

For an impurity in jellium, in order to make sure that $V_{\text{eff}}(r \rightarrow \infty) = 0$, we must subtract from V_{xc} its constant asymptotic part, $V_{\text{xc}}(r_s)$, r_s being the jellium parameter. Finally, one obtains

$$V_{\text{xc}}(r_s(r)) - V_{\text{xc}}(r_s) = \frac{1}{\alpha} \frac{r_s(r) - r_s}{r_s \cdot r_s(r)} + 0.0225 \ln \left\{ \frac{r_s(r)(r_s + 21)}{r_s(r_s(r) + 21)} \right\} . \quad (\text{II.37})$$

Remarks:

1. In the case of a point charge immersed into jellium, the assumption of a locally constant density is certainly a rough approximation near the impurity. However, since the potential in that region is largely dominated by the Coulomb part, the whole potential V_{eff} remains valid³³.
2. The contribution of the second term of Eq. II.31, $\epsilon_{\text{xc}}^{(2)}$, is small: it has been estimated by Rasolt et al.³⁴ and Singwi et al.³³ applied this result to hydrogen in jellium.
3. The approximation of slowly varying density is not made for the kinetic and electrostatic parts, which are treated exactly.
4. If LDA is applied to $T_s\{n\}$ (Eq. II.26), one recovers the Thomas-Fermi equations.
5. The extension of the theory to finite temperatures is straightforward³⁵.
6. The local density theory can be extended also to the spin polarized case^{29,36} by enlarging the density variable to include unequal local spin densities (Local Spin Density Approximation: LSDA).

III. SOLUTION TO THE DFF EQUATIONS

1. The scattering problem

As shown in Sec.II, the problem of a positive point charge in jellium can be reduced within an exact scheme to solving a one-body Schrödinger equation. The wave functions to be determined correspond to some pseudo-particles moving in an effective potential which depends itself upon the density. Self-consistency is therefore of crucial importance. If the index i contains all relevant quantum numbers, one has

$$\left(-\frac{1}{2}\Delta + V_{\text{eff}}\right)\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) . \quad (\text{III.1})$$

In the case of an impurity in jellium, the effective potential (see Eq. II.28) is spherically symmetric and consists of two parts:

$$V_{\text{eff}}(n(r), r) = V_{\text{es}}(r) + V_{\text{xc}}(n(r)) . \quad (\text{III.2})$$

The exchange-correlation potential V_{xc} is given by Eq. (II.37), and the electrostatic part contains the usual Coulomb interactions

$$V_{\text{es}}(r) = -\frac{1}{r} + \int d\vec{r}' \frac{\Delta n(r')}{|\vec{r}-\vec{r}'|} , \quad (\text{III.3})$$

where $\Delta n(r)$ stands for $n(r)-n_0$. By expanding $1/|\vec{r}-\vec{r}'|$ in Legendre polynomials, Eq. III.3 can be rewritten in the convenient form:

$$V_{\text{es}}(r) = 4\pi \int_r^\infty dr' r' \Delta n(r') - \frac{4\pi}{r} \int_0^\infty dr' r'^2 \Delta n(r') . \quad (\text{III.4})$$

The relevant quantity is the electron density, given by a sum over the partial densities $|\psi_i(\vec{r})|^2$ up to the Fermi level (see Eq.II.30). The Fermi wave-vector k_F is related to the jellium parameter r_s by

$$k_F^3 = \frac{9\pi}{4} r_s^{-3} . \quad (\text{III.5})$$

The solution to Eq.III.1 concerns elementary scattering theory. Using the spherical symmetry of the problem, the wave functions Ψ can be split into

$$\psi_{\mathbf{k}}(\vec{\mathbf{r}}) = \sum_{\ell} \frac{1}{r} u_{\mathbf{k},\ell}(r) P_{\ell}(\cos\theta) , \quad (\text{III.6})$$

where the P_{ℓ} 's are the Legendre polynomials and contain all the angular dependence. The differential equation for the radial part is easily found to be

$$u''_{\mathbf{k},\ell}(r) + \left\{ k^2 - \frac{\ell(\ell+1)}{r^2} - 2V_{\text{eff}}(r) \right\} u_{\mathbf{k},\ell}(r) = 0 , \quad (\text{III.7})$$

with the well-known boundary conditions:

$$u_{\mathbf{k},\ell}(r \rightarrow 0) = c r^{\ell+1} , \quad (\text{III.8})$$

and

$$u_{\mathbf{k},\ell}(r \rightarrow \infty) = c' \frac{1}{k^2} \sin\left\{ kr - \frac{\ell\pi}{2} + \delta_{\ell}(k) \right\} , \quad (\text{III.9})$$

where c and c' are some normalization constants, and $\delta_{\ell}(k)$ the phase shifts.

In addition to the scattering states, characterized by the asymptotic condition (III.9), bound states may occur. Their existence and their number can be determined from Levinson's theorem, which gives an exact relationship between the number N_{ℓ} of bound states with angular momentum ℓ and the zero-energy phase shifts:

$$N_{\ell} = \frac{1}{\pi} \lim_{k \rightarrow 0} \delta_{\ell}(k) . \quad (\text{III.10})$$

The $(2\ell+1)$ degeneracy is not taken into account. Various demonstrations of Levinson's theorem can be found in the literature (see e.g. ref 37).

Remark:

Two bound states (one for each spin direction) occur as soon as $r_{\text{S}} > 1.9$, i.e. for all metallic densities except Be. It should

be recalled that, within the density functional formalism, only the total charge density (including the scattering and bound state contributions $n(r)=n_{sc}(r)+n_b(r)$) describes the ground state electron density of the inhomogeneous interacting electron gas. In addition, the Bohr radius of these pseudo-particle bound states is much larger than the inter-ionic spacing. A physical investigation of bond formation cannot be made unless the band structure is taken into account.

a) Scattering states

The computation of the scattering states can be done within two different approaches:

1) in the elegant "variable phase approach"³⁷, the second order linear differential equation for the radial part of the wave function (Eq.III.7) is shown to be equivalent to a first-order non-linear differential equation for the phase shifts, called the phase equation:

$$\frac{\partial}{\partial r} \delta_\ell(k, r) = -\frac{2}{k} V_{eff}(r) \{ \cos \delta_\ell(k, r) \hat{j}_\ell(kr) - \sin \delta_\ell(k, r) \hat{n}_\ell(kr) \}^2, \quad (III.11)$$

with boundary condition

$$\delta_\ell(k, r \rightarrow 0) = 0. \quad (III.12)$$

$\hat{j}_\ell$ and $\hat{n}_\ell$ are the Riccati-Bessel functions (see Appendix A), and the usual phase shifts $\delta_\ell(k)$ can be shown to correspond to the asymptotic value:

$$\delta_\ell(k) = \lim_{r \rightarrow \infty} \delta_\ell(k, r). \quad (III.13)$$

The phase shifts are fully determined by Eqs. III.11 and

III.12, so that no mod(π) ambiguity exists, as is the case in the conventional approach (see below).

Once the phase functions $\delta_\ell(k, r)$ are known, the radial part $u_{k, \ell}(r)$ of the wave function and its first derivative are given by

$$u_{k, \ell}(r) = \alpha_\ell(r) \{ \cos \delta_\ell(k, r) \hat{j}_\ell(kr) - \sin \delta_\ell(k, r) \hat{n}_\ell(kr) \}, \quad (\text{III.14})$$

$$u'_{k, \ell}(r) = k \alpha_\ell(r) \{ \cos \delta_\ell(k, r) \hat{j}'_\ell(kr) - \sin \delta_\ell(k, r) \hat{n}'_\ell(kr) \} \quad (\text{III.15})$$

where the prime denotes the derivative with respect to the argument. The amplitude function $\alpha_\ell(r)$ is given by

$$\ln \alpha_\ell(r) = - \frac{2}{k} \int_0^r ds v_{\text{eff}}(s) \{ \cos \delta_\ell(k, s) \hat{j}_\ell(ks) - \sin \delta_\ell(k, s) \hat{n}_\ell(ks) \} \{ \sin \delta_\ell(k, s) \hat{j}_\ell(ks) + \cos \delta_\ell(k, s) \hat{n}_\ell(ks) \} \quad (\text{III.16})$$

Remarks:

1. This shows that $u_{k, \ell}(r)$ can be decomposed into an always positive amplitude (the potential distorts the radial part of the wave function) and a variable phase (the potential creates phase shifts).
2. It can be shown that $\alpha'_\ell(r)$ is positive (negative) if v_{eff} is negative (positive), i.e. the potential attracts or repels the wave function.
3. The amplitude function $\alpha_\ell(r)$ coincides with the modulus of the Jost function created by the potential truncated at r .

Finally, the whole wave function $\Psi_k(\vec{r})$ is given by

$$\Psi_k(\vec{r}) = \frac{1}{kr} \sum_{\ell} (2\ell+1) i^\ell e^{i\delta_\ell} \frac{u_{k, \ell}(r)}{\alpha_\ell(\infty)} P_\ell(\cos\theta), \quad (\text{III.17})$$

and the scattering perturbed charge density by

$$\begin{aligned} \Delta n_{\text{sc}}(r) &= n_{\text{sc}}(r) - n_0 \\ &= \pi^{-2} \int_0^{k_F} dk \sum_{\ell} (2\ell+1) \frac{1}{r} \left\{ \left| \frac{u_{k, \ell}(r)}{\alpha_\ell(\infty)} \right|^2 - |\hat{j}_\ell(kr)|^2 \right\}. \end{aligned} \quad (\text{III.18})$$

One of the advantages of this method is to give the phase shifts without having to calculate first the wave functions. Thus, one obtains very quickly the number of bound states (see Eq.III.10) and can check the total displaced charge Z via Friedel sum rule:

$$Z = \frac{2}{\pi} \sum_{\ell} (2\ell+1) \delta_{\ell}(k_F) . \quad (\text{III.19})$$

However, this method requires more computing time than the direct integration of Eq. III.7 . Further, the phase function has a very pronounced step-like behavior for $\ell = 0$ and $k \rightarrow 0$ since $1s$ -type bound states occur. The abrupt change in $\delta_0(k \rightarrow 0, r)$ requires a sophisticated numerical treatment.

ii) In the conventional approach to scattering problems, one rewrites the asymptotic condition for $u_{k,\ell}(r)$, Eq. III.9 , as:

$$u_{k,\ell}(r \rightarrow \infty) = \alpha_{\ell} \{ \cos \delta_{\ell}(k) \hat{j}_{\ell}(kr) - \sin \delta_{\ell}(k) \hat{n}_{\ell}(kr) \} . \quad (\text{III.20})$$

Then, the solutions to Eq. III.7 are computed directly up to a radius R where the potential is set equal to zero and the solution matched to that of the free electron case:

$$\left. \frac{d}{dr} \ln u_{k,\ell}(r) \right|_{r=R} \equiv \phi = \frac{\cos \delta_{\ell}(k) \hat{j}'_{\ell}(kr) - \sin \delta_{\ell}(k) \hat{n}'_{\ell}(kr)}{\cos \delta_{\ell}(k) \hat{j}_{\ell}(kr) - \sin \delta_{\ell}(k) \hat{n}_{\ell}(kr)} \Bigg|_{r=R} , \quad (\text{III.21})$$

and the phase shifts are then given by

$$\tan \delta_{\ell}(k) = \frac{\hat{j}'_{\ell}(kr) - \phi \hat{j}_{\ell}(kr)}{\hat{n}'_{\ell}(kr) - \phi \hat{n}_{\ell}(kr)} \Bigg|_{r=R} , \quad (\text{III.22})$$

where the prime denotes the derivivative with respect to the argument. Finally, the normalization constant α_{ℓ} is obtained from Eq. III.20 :

$$\alpha_{\ell} = \frac{u_{k,\ell}(R)}{\cos \delta_{\ell}(k) \hat{j}_{\ell}(kr) - \sin \delta_{\ell}(k) \hat{n}_{\ell}(kr)} , \quad (\text{III.23})$$

and the normalized wave function is $u_{k,\ell}(r)/\alpha_\ell$.

The contribution of the scattering states to the charge density is of course given by Eq. III.18 with the obvious equivalence between $\alpha_\ell(\infty)$ and α_ℓ .

The k - and ℓ - dependence of the phase shifts is shown in Table I for Al ($r_s = 2.07$) and Cs ($r_s = 5.63$). The limiting value $\delta_0(k \rightarrow 0)$ shows the presence of a 1s bound state in both cases.

k/k_F	Al					Cs				
	δ_0	$10^1 \delta_1$	$10^2 \delta_2$	$10^3 \delta_3$	$10^4 \delta_4$	δ_0	$10^1 \delta_1$	$10^2 \delta_2$	$10^3 \delta_3$	$10^4 \delta_4$
0.980	1.08	1.16	1.97	3.54	0.65	1.82	-1.11	-1.39	-15.0	-1.18
0.915	1.11	1.04	1.60	2.62	0.44	1.87	-0.93	-1.55	-15.9	-1.02
0.810	1.15	0.84	1.08	1.46	0.24	1.96	-0.71	-1.92	-15.2	-0.67
0.676	1.22	0.59	0.57	0.64	0.19	2.08	-0.54	-2.18	-10.2	-0.18
0.525	1.30	0.33	0.21	0.14	0.08	2.22	-0.47	-1.54	-2.6	0.03
0.373	1.41	0.14	0.06	0.08	0.01	2.40	-0.32	-0.41	-0.9	0.01
0.232	1.54	0.04	0.03	.	.	2.64	-0.10	-0.03	0.3	.
0.117	1.73	0.01	.	.	.	2.87	.	.	.	.
0.037	2.20	.	.	.	.	3.06	.	.	.	.
0.001	3.09	10^{-7}	10^{-11}	10^{-15}	10^{-21}	3.14	10^{-7}	10^{-12}	10^{-13}	10^{-20}

TABLE I. Phase shifts $\delta_\ell(k)$ with $\ell=0$ to $\ell=4$ in the cases of Al and Cs. The negative values appearing for Cs are due to the very large oscillations of the effective potential V_{eff} responsible for the large Friedel oscillations of $\Delta n(r)$ (see Fig.3). In both cases, $\delta_0(k \rightarrow 0) = \pi$, indicating the presence of bound states (see Eq.III.10).

b) Bound states

As already mentioned, 1s bound states occur for all metallic densities with $r_s > 1.9$. They can be computed without major difficulty by direct integration of Eq. III.7 with $\ell = 0$ and k^2 replaced by E_{1s} . The bound states are filled with two pseudo-particles, so that the bound state density is

$$n_b(r) = 2 |\psi_{1s}(\vec{r})|^2 = \frac{1}{2\pi} \frac{|u_{\ell=0}(r)|^2}{Ar^2} \quad (\text{III.24})$$

where

$$A = \int_0^\infty dr |u_{\ell=0}(r)|^2. \quad (\text{III.25})$$

The full perturbed charge density is finally given by

$$\Delta n(r) = n_{sc}(r) - n_0 + n_b(r). \quad (\text{III.26})$$

2. The first approximate solution

Since the effective potential V_{eff} depends on the density $n(r)$, a self-consistent solution is needed for the system of equations (III.1), (III.2) and (III.26). One starts the procedure by assuming some screened potential for V_{eff} , solves the Schrödinger equation (III.1), determines the density through Eq. III.26, and builds a new effective potential using Eq. III.2. One has to iterate this procedure until the charge density obtained at iteration (i) is equal to the one used to build the effective potential, i.e. until

$$n^{(i)}(r) = n^{(i-1)}(r), \text{ for all } r. \quad (\text{III.27})$$

For each iteration, one needs typically 7 or 8 partial waves and some 40 points for the k -integration (Eq. III.18). This implies that the scattering problem described in Sec. III.1 has to be solved about 300 times for each iteration. Unfortunately, the condition (III.27) is never fulfilled, and the direct iteration does not converge: the density $n^{(i)}(r)$ always oscillates around the self-consistent solution $n^{sc}(r)$, and is not stable³⁹ (dependence on the initial guess for V_{eff}).

The first approximate solution was proposed by Popovic and Stott¹⁸, who suggested using a two parameter potential for V_{eff} :

$$V_{\alpha\beta}(r) = -\frac{1}{r} e^{-\alpha r^\beta} . \quad (\text{III.28})$$

The solution was assumed to be self-consistent if α and β were chosen in such a way that Friedel sum rule (Eq. III.19) was fulfilled with both the trial potential $V_{\alpha\beta}$ and the effective potential built after one iteration.

Following Popovic and Stott, we have calculated this two parameter potential for various densities of the electron gas. This approximate solution leads to surprisingly good results for high densities of the electron gas (e.g. Al or Mg), but fails for low densities ($r_s > 3.0$): the absence of iterations using the exchange-correlation potential generates errors which increase with r_s . Further, in the case of low densities of the electron gas, the lack of electrons increases the screening distance and makes of $V_{\alpha\beta}$ too poor an approximation for V_{eff} . As a result, the Friedel oscillations are out of phase, and the contact density is overestimated by a large amount. This is illustrated in Fig. 1, where the fully self-consistent curve (full line) is compared to the approximate solution obtained from the procedure of Popovic and Stott, in the extreme case of Cs ($r_s = 5.63$).

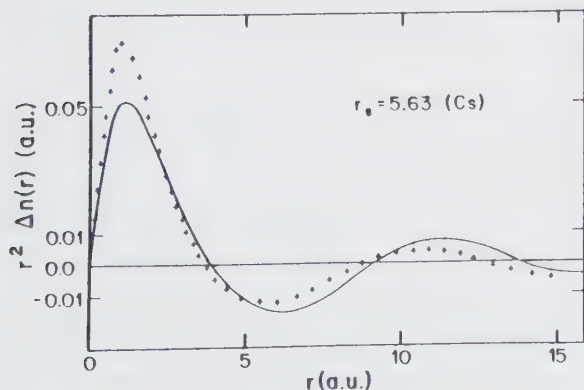


Fig 1. Comparison between the fully self-consistent charge density (full line) and the result obtained from the method of Popovic and Stott¹⁸ (crosses) in the case of Cs, the metal with lowest electron density.

In addition, it should be mentioned that for high r_s -values, it becomes very difficult to find values of α and β which fulfill the requirement of charge conservation with satisfactory precision.

3. The fully self-consistent density

The problem of the convergence of the fully self-consistent equations was solved by Manninen et al.³⁸, who proposed two tricks which assure convergence for all metallic densities.

a) Additional screening

The electrostatic part of V_{eff} requires at each iteration (i) the solution of the Poisson equation

$$\Delta V_{\text{es}}^{(i)}(r) = -4\pi n^{(i)}(r) \quad , \quad (\text{III.29})$$

which leads to the long-ranged integral:

$$V_{\text{es}}^{(i)}(r) = \int d\vec{r}' \frac{n^{(i)}(r')}{|\vec{r}-\vec{r}'|} \quad . \quad (\text{III.30})$$

By subtracting from both sides of Eq. III.29 the term $q^2 V_{\text{es}}^{(i)}$ (where q is a real constant), and replacing on the r.h.s. $V_{\text{es}}^{(i)}$ by $V_{\text{es}}^{(i-1)}$, Eq. III.29 is transformed into a Helmholtz-type equation, the solution to which is nicely convergent:

$$V_{\text{es}}^{(i)}(r) = \int d\vec{r}' \frac{e^{-q|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \{n^{(i)}(r') - \frac{q^2}{4\pi} V_{\text{es}}^{(i-1)}(r')\} \quad . \quad (\text{III.31})$$

It can be shown³⁹ that the best choice for q is the Thomas-Fermi screening length:

$$q^2 = k_{\text{TF}}^2 = \frac{4k_F}{\pi} \quad . \quad (\text{III.32})$$

b) Feedback

The second trick uses a feedback technique which prevents too large oscillations of $n^{(i)}(r)$ around the self-consistent solution $n^{\text{SC}}(r)$ from occurring. Instead of writing, for iteration (i):

$$V_{\text{eff}}^{(i)} = V_{\text{es}}^{(i)} + V_{\text{xc}}^{(i)}, \quad (\text{III.33})$$

one uses the effective potential obtained from iteration (i-1) and writes

$$V_{\text{eff}}^{(i)} = \alpha \{ V_{\text{es}}^{(i)} + V_{\text{xc}}^{(i)} \} + (1-\alpha) V_{\text{eff}}^{(i-1)}. \quad (\text{III.34})$$

α should be chosen close to 1 for high densities of the electron gas, where the convergence is rapid, and around 0.5 for very low densities. The final result being independent of α , one can even speed up the convergence by making α r-dependent.

When using these two tricks, the system of equations (III.1), (III.2) and (III.26) converges for all densities of the electron gas. However, the solution still requires large programming efforts and computing times.

We have calculated the perturbed charge density for $r_s = 2.0, 2.2, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5$, and 6.0 . Eq. III.1 was solved up to a radius R larger than $6r_s$ using Numerov method⁴⁰ (see Appendix B) for partial waves up to $l = 8$. The density $n(r)$ has been integrated using a gaussian integration formula with 50 steps. The Numerov method was also used for bound states, which are very shallow for high densities of the electron gas ($r_s \approx 2$) as can be seen from Fig. 2.

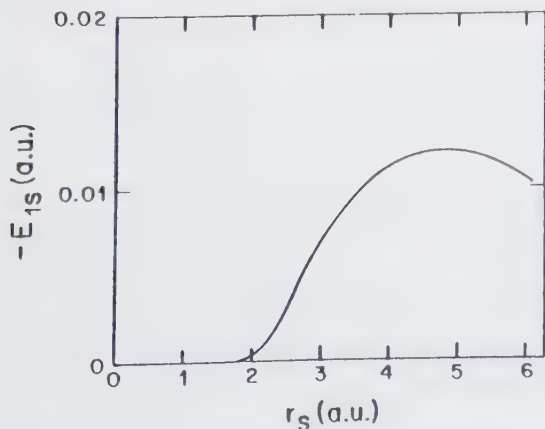


Fig. 2. Energy of the 1s bound state for a point charge ($Z=1$) in jellium versus the parameter r_s .

Even for bound states energies smaller than 0.001 a.u., the contribution of $n_b(r)$ to the full density is non negligible (in particular for r close to the origin).

Thanks to the computing facilities available, we could iterate the solution a very large number of times (more than a hundred iterations for large r_s -values) to make sure that convergence was achieved at every point. The iteration procedure was started by assuming a screened Coulomb potential (Hulthén potential⁴¹) as initial V_{eff} . After a few iterations, the value of the charge density at the origin as well as the first maximum of $r^2\Delta n(r)$ were already within a few percent of their final values. Further iterations then changed the extrema of the Friedel oscillations and the self-consistency of $\Delta n(r)$ was built up gradually from 0 to larger r -values. To achieve convergence also at the extrema of further Friedel oscillations, a large number of iterations was needed for $r_s > 3.5$. This is due to the more pronounced influence of the exchange-correlation potential as compared to the high density region where the rapidly oscillating densities could be determined fully self-consistently after 20 or 30 iterations. As examples, the self-consistent charge densities $r^2\Delta n(r)$ in the extreme cases of Al ($r_s=2.07$) and Cs ($r_s=5.63$) are shown in Fig 3.

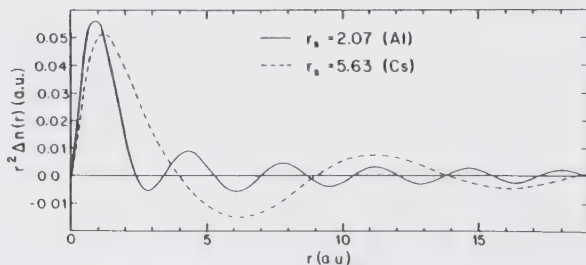


Fig. 3. Comparison between self-consistent charge densities around a point charge ($Z=1$) in jellium for very high (Al) and very low (Cs) densities of the electron gas.

In order to allow easier use for further applications, we found it convenient to parametrize⁴² the resulting self-consistent densities, using a simple analytic expression which contains only r_s as input parameter.

4. Parametrization of $\Delta n(r)$

It is known that the charge density $\Delta n(r) = n(r) - n_0$ fulfills three conditions:

- charge conservation: $\int d\vec{r} \Delta n(r) = 1$, (III.35)

- asymptotic behavior (see Appendix C):

$$\Delta n(r \rightarrow \infty) = \Lambda \frac{\cos(2k_F r + \phi)}{r^3} + O\left(\frac{1}{r^4}\right), \quad (\text{III.36})$$

- cusp condition : $\left. \frac{d}{dr} \Delta n(r) \right|_{r=0} = -2\Delta n(0)$. (III.37)

The last condition (III.37) is a direct consequence of the Schrödinger equation, and is valid for each individual partial wave as long as the potential behaves as $-1/r$ close to the origin, which is the case in the local density approximation.

A convenient parametrization of $\Delta n(r)$ can be obtained using the following function:

$$\Delta n(r) = \frac{1}{\pi} e^{-2r} + \left\{ \Delta n(0) - \frac{1}{\pi} \right\} e^{-2r(1+r)} + f(2k_F r) , \quad (\text{III.38})$$

which consists of the hydrogen 1s-state density, a contribution giving the correct density and slope at the origin, and a function f which accounts for the oscillations. Eqs. III.36 and

III.37 imply that f must be chosen in such a way that $f(0) = f'(0) = 0$, and $f(r \rightarrow \infty) = \Lambda \cos(2k_F r + \phi)/r^3$. A possible choice for f is a combination of Riccati-Bessel functions (see Appendix A). We exploited the fact that the zeros of f are strictly linear functions of r_s to parametrize separately the regions $r < Z_2$ and $r > Z_2$, Z_2 being the second zero of f , given

by

$$z_2 = 1.52 r_s + 0.4644 . \quad (\text{III.39})$$

The parametrized form was chosen (with x standing for $2k_F r$) as

$$r < z_2: f(x) = \frac{A_0}{x^4+1} \hat{j}_0(x) \{1-e^{-x}\} + \frac{1}{x^3+1} \sum_{\ell=1}^3 A_\ell \hat{j}_\ell(x) \quad (\text{III.40})$$

$$r > z_2: f(x) = \frac{1}{x^3+1} \sum_{\ell=2}^5 B_\ell \hat{j}_\ell(x) .$$

We are left with a number of parameters which have to be expressed as functions of r_s : the contact density $\Delta n(0)$, and the amplitudes A_ℓ and B_ℓ .

The behavior of the contact density is shown in Fig.4. Since

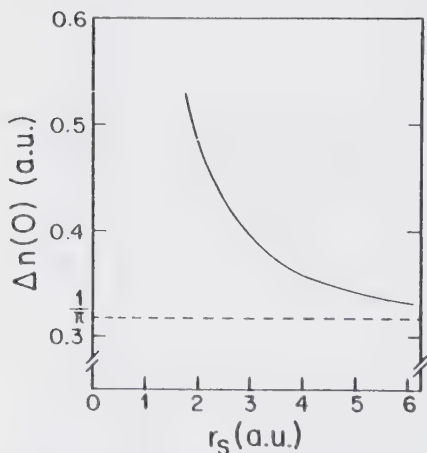


Fig. 4. Contact density $\Delta n(0)=n(0)-n_0$ at the impurity versus the jellium parameter r_s .

one expects that for large values of r_s the contact density approaches that of hydrogen, it is natural to parametrize $\Delta n(0)$ by a function that tends asymptotically towards $1/\pi$. An inspection of a log-log plot of $\Delta n(0)-1/\pi$ versus r_s indicates that a very good parametrization in the range $1.8 \leq r_s \leq 6.0$ is given by

$$\Delta n(0) = \frac{1}{\pi} + \exp\{-0.72 - 1.28 \ln(r_s) - 0.385 \ln^2(r_s)\} \quad (\text{III.41})$$

The amplitudes A_ℓ and B_ℓ are smooth functions of r_s as shown in Figs. 5A and 5B. Their values, in the range $2.0 < r_s < 6.0$, have been fitted to a power series in $1/r_s$, which is given in Table II.

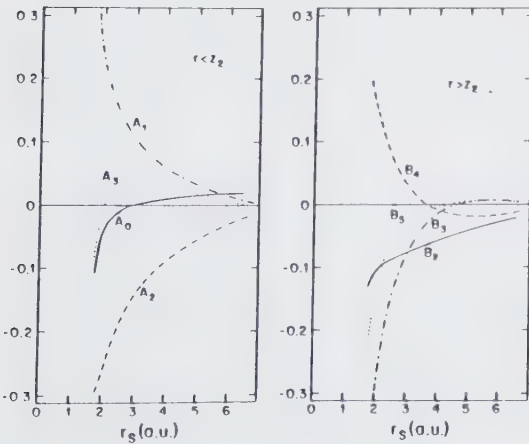
a) $r < r_2$: $\Lambda_\ell = a_\ell/r_s^4 + b_\ell/r_s^3 + c_\ell/r_s^2 + d_\ell/r_s + e_\ell$

ℓ	a_ℓ	b_ℓ	c_ℓ	d_ℓ	e_ℓ
0	- 9.879	10.795	- 4.422	0.696	- 0.018
1	0.347	2.257	- 1.711	0.927	- 0.103
2	14.900	- 20.780	10.200	- 2.769	0.233
3	- 15.040	17.681	- 8.380	1.946	- 0.156

b) $r > r_2$: $B_\ell = a_\ell/r_s^4 + b_\ell/r_s^3 + c_\ell/r_s^2 + d_\ell/r_s + e_\ell$

ℓ	a_ℓ	b_ℓ	c_ℓ	d_ℓ	e_ℓ
2	- 6.197	5.882	- 1.256	- 0.379	0.047
3	- 4.056	6.326	- 6.186	1.631	- 0.120
4	2.388	- 6.313	6.083	- 1.688	0.122
5	- 16.430	19.463	- 9.391	1.820	- 0.114

TABLE II. Amplitudes of the parametric form for the perturbed charge density as functions of r_s .



Figs. 5A and 5B. Behavior of the amplitudes Λ_ℓ and B_ℓ (see Eq. III.40) as functions of r_s . They can be fitted to a series in inverse powers of r_s (see Table II).

The precision of the fit is illustrated in Fig. 6 which shows the self-consistent curve and the parametrized function on the same graph in the case of Au ($r_s = 3.0$).

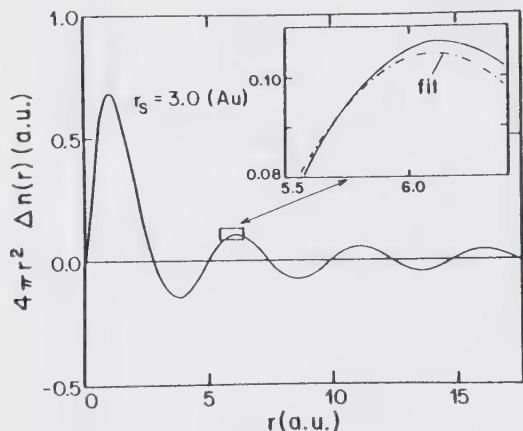


Fig. 6. Plots of the fully self-consistent charge density around an impurity in jellium with $r_s = 3.0$ (Au), and of the density obtained from the parametrized form (Eqs. III.38 and III.40). Both curves can be distinguished only in the insert.

The electron densities obtained from the parametrized form have been compared to the results of other authors^{33,39,43,44}, and good agreement has always been found. Excellent agreement also exists between the Fourier transforms of the calculated $\Delta n(r)$ and that of the parametrized expression. Furthermore, the total displaced charge (Eq. III.35) calculated with the values from Table II was found to be very close to 1 for all values of r_s from 1.8 to 6.0.

We also investigated the effect on the charge density of the choice of the parametrized form for the exchange-correlation potential V_{xc} . We repeated the calculation with $r_s = 4.0$ using the Wigner formula²⁶, and found a small difference in the amplitude of the first two oscillations of $r^2 \Delta n(r)$. This difference was larger than the one existing between the self-consistent result and the parametrized form.

We also calculated energies (see next section) using both the

numerical values and the parametrized form. The values found for various positions of the impurity and various hosts were found to differ from each other by a few percent only (7% in the worst case).

IV. CALCULATION OF THE ENERGY

1. Evaluation of $E(\vec{R}_\mu)$

Once the perturbed charge density is determined, the lattice ions are introduced into the jellium at the lattice sites $\vec{R}_\ell$, and the positive background removed. In first order perturbation theory, the energy of an impurity at $\vec{R}_\mu$ is given by (see Eq. I.3)

$$E(\vec{R}_\mu) = \sum_{\ell} \left\{ \frac{Z}{|\vec{R}_\mu - \vec{R}_\ell|} + \int d\vec{r} \Delta n(\vec{r} - \vec{R}_\mu) W(\vec{r} - \vec{R}_\ell) \right\}. \quad (IV.1)$$

The first term contains the impurity-ion Coulomb repulsion, and the second the interaction between the perturbed charge density around the muon and the pseudopotential W .

Since the total displaced charge is equal to 1, Eq. IV.1 can be rewritten as

$$E(\vec{R}_\mu) = \sum_{\ell} \int d\vec{r} \Delta n(\vec{r}) \left\{ \frac{Z}{|\vec{R}_\mu - \vec{R}_\ell|} + W(\vec{r} + \vec{R}_\mu - \vec{R}_\ell) \right\}. \quad (IV.2)$$

All pseudopotentials (see Sec. IV.2) show a long ranged behavior $W(r) = -Z/r$ for r exceeding some core radius r_c . Therefore, the two terms in the brackets of Eq. IV.2 cancel each other for r -values smaller than $|\vec{R}_\mu - \vec{R}_\ell| - r_c$. This implies that the interaction is weak if the screening of the impurity is completed within a short distance. The smallest r -value which gives a contribution to the integral in (IV.3) is the one where the first overlap with the pseudopotential core occurs. It is therefore of crucial importance that the displaced charge density $\Delta n(r)$ including its long-ranged oscillations, is calculated accurately.

The first term on the r.h.s. of Eq. IV.1 can be evaluated using Ewald's method⁴⁵ for lattice sums, with the result

$$\sum_{\ell} \frac{Z}{|\vec{R}_\mu - \vec{R}_\ell|} = Z \left\{ \frac{4\pi}{\Omega} \sum_{\vec{g}} \frac{\cos \vec{g} \cdot \vec{R}_\mu}{g^2} e^{-g^2/4G^2} + \sum_{\ell} \frac{1}{|\vec{R}_\mu - \vec{R}_\ell|} \operatorname{erfc}(G|\vec{R}_\mu - \vec{R}_\ell|) \right\} \quad (IV.3)$$

where G can be chosen in such a way that both sums converge rapidly. $\vec{g}$ is a reciprocal lattice vector and Ω the atomic volume.

The calculation of the second term of Eq. IV.1 is straightforward in Fourier space and leads to

$$\sum_{\vec{\ell}} \int d\vec{r} \Delta n(\vec{r} - \vec{R}_{\mu}) W(\vec{r} - \vec{R}_{\ell}) = \frac{1}{\Omega} \sum_{\vec{g}} \cos(\vec{g} \cdot \vec{R}_{\mu}) \Delta n(\vec{g}) W(\vec{g}) , \quad (\text{IV.4})$$

where it has been assumed that $W(\vec{g}) = W(-\vec{g})$ (see Sec. IV.2).

Using the fact that the pseudopotentials can always be written in reciprocal space as

$$W(\vec{g}) = - \frac{4\pi Z}{g^2} f(\vec{g}) , \quad (\text{IV.5})$$

where $f(\vec{g})$ is an even function of $\vec{g}$ and $f(0) = 1$, one can calculate the contributions of the term $\vec{g} = \vec{0}$ in Eqs. IV.3 and IV.4

$$\text{Eq. (IV.3) } (g \rightarrow 0) = \frac{4\pi Z}{\Omega} \frac{\cos \vec{g} \cdot \vec{R}_{\mu}}{g^2} e^{-g^2/4G^2} , \quad (\text{IV.6})$$

$$\text{Eq. (IV.4) } (g \rightarrow 0) = - \frac{4\pi Z}{\Omega} \frac{\cos \vec{g} \cdot \vec{R}_{\mu}}{g^2} , \quad (\text{IV.7})$$

so that the terms containing $\vec{g} = \vec{0}$ reduce to the constant $-\pi/(\Omega G^2)$. Thus, Eq. IV.1 can be split into two parts:

$$E(\vec{R}_{\mu}) = E_{\text{str}}(\vec{R}_{\mu}) + E_{\text{int}}(\vec{R}_{\mu}) . \quad (\text{IV.8})$$

a) The first part, E_{str} , depends only on the lattice structure:

$$E_{\text{str}}(\vec{R}_{\mu}) = Z \left\{ \sum_{\vec{\ell}} \frac{1}{|\vec{R}_{\mu} - \vec{R}_{\ell}|} \operatorname{erfc}(G|\vec{R}_{\mu} - \vec{R}_{\ell}|) + \frac{4\pi}{\Omega} \sum_{\vec{g}} \frac{\cos \vec{g} \cdot \vec{R}_{\mu}}{g^2} e^{-g^2/4G^2} - \pi/(\Omega G^2) \right\}$$

$$= Z \frac{a_B}{a} \chi(\vec{R}_{\mu}) \quad (\text{IV.9})$$

$X(\vec{R}_\mu)$ is related to the Madelung energy $M(\vec{R}_\mu)$, defined²⁰ as:

$$E_{\text{str}}(\vec{R}_\mu) = \frac{Z^{2/3}}{r_s} M(\vec{R}_\mu). \quad (\text{IV.10})$$

Since a is $r_s Z^{1/3} \left(\frac{3}{4\pi n}\right)^{-1/3}$ ($n=2$ for bcc, $n=4$ for fcc), $X(\vec{R}_\mu)$ and $M(\vec{R}_\mu)$ differ only by a constant.

$X(\vec{R}_\mu)$ is plotted in Fig.7 for $\vec{R}_\mu$ moving along a straight line from the octahedral (O) to the tetrahedral (T) sites in the bcc, fcc and hcp lattices. It can

be seen that the emptiest lattice (bcc) is the one where E_{str} is the smallest. Another feature should be mentioned: we have calculated⁴⁶ the volume of a sphere that fits into the space left at various sites by touching spheres centered at the lattice points. In the fcc lattice, the volume V_o at the octahedral site is 6.2 times larger than the volume V_t at the tetrahedral site. In the hcp case (with ideal c/a ratio), $V_o = 6.3 V_t$. But in the bcc lattice, $V_o = \frac{1}{6.7} V_t$. It follows from these simple considerations that the structural part of the energy is minimum where the maximum space is available.

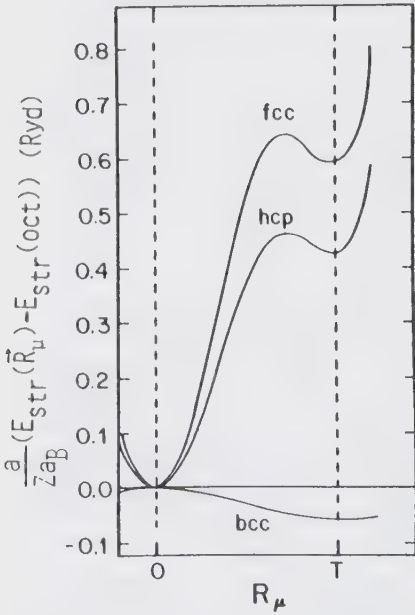


Fig. 7. Part of the energy depending only on the structure (Eq. IV.9) for bcc, fcc and hcp (ideal c/a) lattices.

b) The second term of Eq. IV.8, which also depends on the lattice structure, contains all interactions between electrons. We therefore called it the interaction part of the energy:

$$E_{\text{int}}(\vec{R}_\mu) = z \frac{1}{\Omega} \sum_g' \cos(\vec{g} \cdot \vec{R}_\mu) \Delta n(g) W(g) . \quad (\text{IV.11})$$

As already discussed above, E_{int} largely compensates E_{str} if the impurity is screened over distances short compared to the nearest neighbour distance. This is the case in metals with small r_s -values (see e.g. Fig.3) which happen to crystallize in the fcc or the hcp structures. On the other hand, in metals with low density of the electron gas (large r_s), which are the bcc metals, the main part of the energy is given by E_{str} . Examples will be mentioned in Sec.V.

2. Pseudopotentials

A pseudopotential is an approximation to the real potential felt by an electron in a solid. This potential is in general weak in metals, in particular in simple metals, which therefore allows a treatment in perturbation theory. The picture of the electron-ion interaction can be schematically described in the following way: electrons in a solid experience a potential made up of two components. In (or near) the ion cores, they feel a strong atomic potential (and their wave functions are very much like those of electrons bound in individual atoms). Between the cores, the electrons see an almost constant potential (and the corresponding wave functions are then nearly plane waves). This behavior led Herring⁴⁷ to treat the electrons in a crystal as a linear combination of core states and of plane waves which he made orthogonal to the filled core states. In the late 1950's, Phillips and Kleinman⁴⁸ showed that this effect can be simulated by a potential having two components: a core potential V_C and a repulsive potential V_R , which cancels most of V_C . In terms of wave functions, this can be understood if one assumes that the real electron wave function ψ has a smooth part ϕ (expanded in plane waves) and a core part (expanded in core states):

$$\psi = \phi + \sum_c b_c \phi_c . \quad (\text{IV.12})$$

The coefficients b_c are obtained from the orthogonalization of ψ to the core states:

$$\langle \phi_c | \psi \rangle = 0 = \langle \phi_c | \phi \rangle + b_c \quad . \quad (\text{IV.13})$$

The wave functions must satisfy the Schrödinger equation

$$\left\{ -\frac{1}{2}\Delta + V_c \right\} \psi = E\psi \quad . \quad (\text{IV.14})$$

Using (IV.12), this equation becomes

$$\left\{ -\frac{1}{2}\Delta + V_c \right\} \phi + \sum_c (E - E_c) \phi_c \langle \phi_c | \phi \rangle = E\phi \quad . \quad (\text{IV.15})$$

The identification of the sum over core states in Eq. IV.15 with an effective repulsive potential V_R is due to Phillips and Kleinman⁴⁸, and Eq. IV.15 finally reads

$$\left\{ -\frac{1}{2}\Delta + V_R + V_c \right\} \phi = E\phi \quad . \quad (\text{IV.16})$$

Thus, the effective potential V_R partially cancels the core potential, leaving a weak pseudopotential as a net result. Cohen and Heine⁴⁹ later showed that this conclusion is quite general and that the cancellation can be made almost complete in the core region.

A good model pseudopotential consists of an ionic Coulomb potential $-Z/r$ for r larger than some core radius r_c . The potential inside the core, for $r < r_c$, is not well defined in many pseudopotentials (see Figs. 8A and 8B), because this lack of information does not cause too many problems for valence electron energy.

However, as mentioned in Sec.I, the different values published for the energies of protons or muons in Al suggest that, in addition to the exact form of the perturbed charge density, the choice of the pseudopotential could be crucially important. The reason for this difficulty is that the energy differences to be calculated are very small.

In order to get a general feeling, we investigated the results obtained from six different local pseudopotentials commonly used in the literature. Five of them are one or two-parameter potentials obtained either from the Ashcroft empty-core pseudopotential or from the simplified Heine-Abarenkov pseudopotential. They differ by an exponential screening in q -space, as q^n . We denote therefore the pseudopotentials with the upper index n .

In Fourier space, these pseudopotentials are

$$W_A^0(q) = -\frac{4\pi Z}{q^2} \cos(qr_c) , \quad (IV.17)$$

which is the bare Ashcroft empty-core pseudopotential, with a screened form :

$$W_A^2(q) = -\frac{4\pi Z}{q^2} \cos(qr_c) e^{-(q/5.5k_F)^2} . \quad (IV.18)$$

Then

$$W_{HA}^0(q) = -\frac{4\pi Z}{q^2} \left\{ \lambda \frac{\sin(qr_c)}{qr_c} + (1-\lambda) \cos(qr_c) \right\} \quad (IV.19)$$

is the bare simplified Heine-Abarenkov pseudopotential, which has two screened forms :

$$W_{HA}^2(q) = -\frac{4\pi Z}{q^2} \left\{ \lambda \frac{\sin(qr_c)}{qr_c} + (1-\lambda) \cos(qr_c) \right\} e^{-(q/5.5k_F)^2} \quad (IV.20)$$

and

$$W_{HA}^4(q) = -\frac{4\pi Z}{q^2} \left\{ \lambda \frac{\sin(qr_c)}{qr_c} + (1-\lambda) \cos(qr_c) \right\} e^{-\xi (q/2k_F)^4} . \quad (IV.21)$$

where $\xi = 0.03$ for all alkali metals and $\xi = 0.15$ for Al.

The last pseudopotential was computed by Borchl and

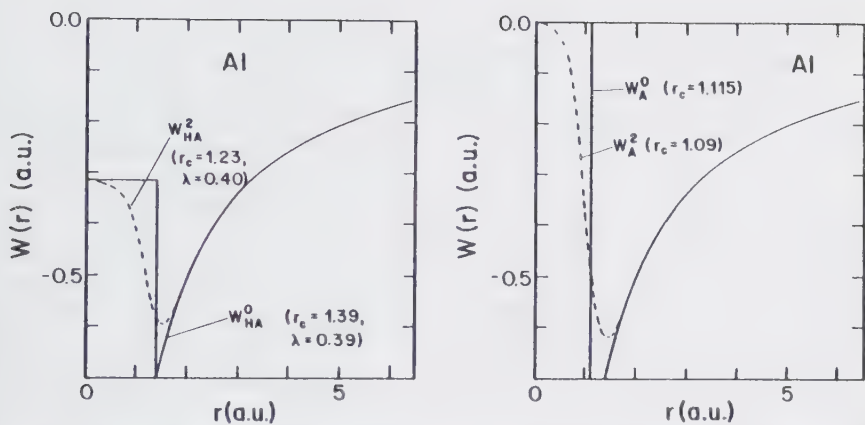
De Gennaro^{50,51} for noble metals, and contains 4 parameters:

$$W_{BG}^0(q) = -\frac{4\pi Z}{q^2} \left(\cos(qr_2) + \frac{\lambda}{q} \left\{ \sin(qr_2) - \sin(qr_1) - qr_2 \cos(qr_2) + \right. \right. \\ \left. \left. qr_1 \cos(qr_1) \right\} - \frac{V_0}{q} \left\{ \sin(qr_1) - qr_1 \cos(qr_1) \right\} \right) . \quad (IV.22)$$

In ref. 51, r_1 has been set equal to 1 a.u. for Cu, Ag and Au, and r_2 chosen in such a way that $r_1 + r_2 = r_1$, the Pauling ionic radius. $W_{BG}^O(r)$ consists of a positive square well with height λ for $r = 0$ to $r = r_1$, then a negative square well with depth V_O for $r = r_1$ to $r = r_2$. For $r > r_2$, $W_{BG}^O(r)$ is the Coulomb potential $-Z/r$.

The parameters r_c and λ in Eqs. IV.17 to IV.21 can be calculated from a variety of experimental properties of the pure solid: transport properties, phonon spectrum, bulk modulus, lattice constant,.... Fixing the parameters of a given pseudopotential to various properties of the metal leads of course to different values for these parameters. A complete list of experimental properties used by various authors would be too long in the present work. Tables III, V and VII (see Secs. V.1, V.2 and V.3) give the parameters used in our calculations, as well as the references to the authors who determined them, for bcc, fcc and hcp simple metals respectively. These tables also contain other parameters of interest for the present calculations: jellium parameter r_s , lattice constant a and valence Z .

The interest of the screening in q -space lies in the fact that all sums over reciprocal lattice vectors (see Eq. IV.11) converge nicely. However, it should be noticed that in direct space, this corresponds to making the pseudopotential a continuous function with continuous derivative. This can be seen in Figs. 8A and 8B, where $W_A^O(r)$ and $W_A^2(r)$, $W_{HA}^O(r)$ and $W_{HA}^O(r)$ are plotted (in the case of Al) (see next page).



Figs. 8A and 8B. Comparison between various pseudopotentials in r -space. The introduction of a screening in q -space modifies the hard-core picture and makes the pseudopotential a continuous function with continuous derivative.

V. RESULTS

1. bcc metals

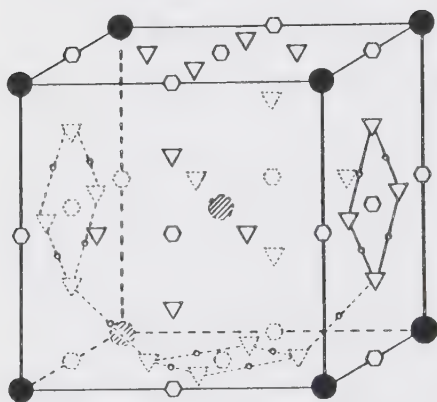


Fig 9. bcc lattice with all octahedral sites (hexagons), all tetrahedral sites (triangles) and some triangular sites (small circles).

The bcc lattice with all symmetric interstitial sites is shown in Fig. 9: the hexagons denote the octahedral sites (O), the triangles the tetrahedral sites (T) and the small circles some of the triangular sites (Tr).

The sites of interest for an interstitial impurity are along the following directions:

from the T-site:

- 1) $\langle 1\ 0\ 0 \rangle$: T-O-T , with distance $d = a/2$ between the two T-sites,
- 2) $\langle 1\ 1\ 0 \rangle$: T-Tr-T, $d = \sqrt{2}\ a/4$,
- 3) $\langle 1\ 1\ 1 \rangle$: T-T , $d = \sqrt{3}\ a/2$,

from the O-site:

- 1) $\langle 1\ 1\ 0 \rangle$: O-O , $d = \sqrt{2}\ a/2$,
- 2) $\langle 1\ 1\ 1 \rangle$: O-O , $d = \sqrt{3}\ a/2$.

We have calculated the potentials along all of these directions using all the pseudopotentials available (see Table III, p.41), for all alkali metals and Ba.

As an example, Fig.10 (p.42) shows the energy profiles in the case of K. Only the curves corresponding to the pseudopotentials predicting the lowest and highest barriers are plotted.

Metal	Z	W_A^0		W_A^2	W_{HA}^0		W_{HA}^2		W_{HA}^4	
r_s	a	ref 52-58		ref 59,60	ref 62,63		ref 59		ref 64,65	
		r_c	r_c	r_c	r_c	λ	r_c	λ	r_c	λ
Li	1	1.038,	1.06,	1.29	1.559	0.408	1.26	-0.070	1.512	0.334
3.253	6.592	1.40,	1.678.		1.562	0.373	1.32	0.081	1.531	0.367
									1.534	0.371
Na	1	1.61,	1.663,	1.53	2.081	0.308	1.50	-0.075	2.071	0.363
3.941	7.984	1.69,	1.758.		2.173	0.480	1.56	0.063	2.116	0.422
K	1	2.047,	2.107,	2.10	3.016	0.572	2.30	0.300	2.972	0.540
4.834	9.874	2.135,	2.226.		3.099	0.624			3.010	0.570
Rb	1	2.02,	2.125,		3.486	0.697			3.384	0.640
5.187	10.554	2.256,	2.40,		3.545	0.727			3.360	0.631
		2.61.								
Cs	1	2.104,	2.16,		3.997	0.768			3.795	0.680
5.628	11.423	2.425,	2.62,		4.114	0.808			3.863	0.709
		2.93.								
Ba	2	2.55								
3.698	9.496									

TABLE III. Pseudopotential parameters for the simple metals crystallizing in the bcc structure with reference to the authors who determined them. The table also contains the jellium parameter r_s , the valence Z and the lattice constant a. All quantities are in a.u..

The dotted line shows the structural part of the energy (Eq.IV.9). The potentials look very similar for all alkali metals: the same site (T) corresponds to a minimum of the energy, and the heights of the barriers are of the same order of magnitude for all elements from Li to Cs. It should be noted that the lowest barriers always coincide with the Ashcroft pseudopotential W_A^0 ,

while the highest barriers correspond to the most screened pseudopotential (W_{HA}^4). For Ba, where the only pseudopotential available is W_A^0 , the barriers are much larger than those of alkali metals.

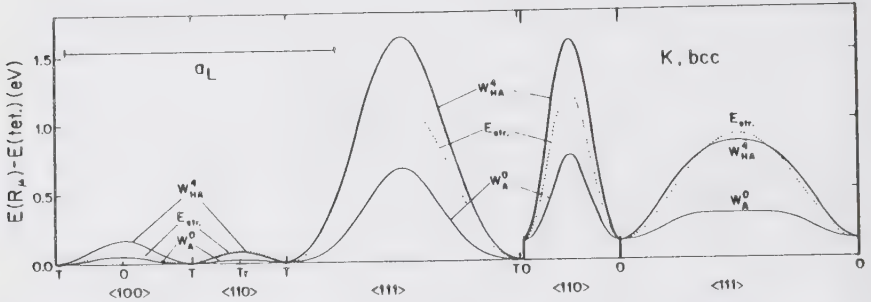


Fig 10: Energy profiles calculated for an impurity in K along straight lines in various directions from a T-site or an O-site. Only the energies corresponding to pseudopotentials predicting the highest and lowest barriers are plotted (solid lines). The dotted line shows the structural part of the energy, and a_L the lattice constant. All energies are given relative to the energy at the T-site which is set equal to 0.

The small heights of the barriers between T-sites, which are of the order of 0.1 to 0.2 eV (Hartree-Fock calculations in Li clusters⁶⁹ give heights of the same order of magnitude) raise the question whether light impurities can be localized at all. The exact calculation of the zero-point motion of muons and protons requires a detailed consideration of the impurity wave function in the real three-dimensional anharmonic potential. In order to get an estimate of the zero-point energy E_0 of a muon or a proton, we have approximated the potentials by a parabola passing through the minimum and the inflection point, and have determined E_0 in the harmonic potential $V(r) = \rho r^2$, which is

$$E_0 = \frac{3}{2} \sqrt{2\rho/m} \quad (V.1)$$

$m = m_\mu$ or m_p is the mass of the impurity in (a.u.) and ρ the curvature of the parabola. This rough estimate makes sense when the obtained values of E_O are either much smaller or much larger than the height H of the barrier, indicating the existence or the nonexistence of an obstacle for diffusion.

Table IV gives the height H and the values of $E_O(\mu)$ and $E_O(p)$ in the cases of K (representative of all alkali metals) and Ba. This table indicates that a proton could be trapped at the T-site in Ba, but not in any alkali metal, at least as far as effects of lattice relaxation are neglected (see Sec.VI.1). On the other hand, a muon cannot be localized in any of these bcc metals.

Direction	K						Ba		
	$H_{\min}$	$E_O(\mu^+)$	$E_O(p^+)$	$H_{\max}$	$E_O(\mu^+)$	$E_O(p^+)$	H	$E_O(\mu^+)$	$E_O(p^+)$
$\langle 100 \rangle, T-O-T$	0.045	0.06	0.02	0.160	0.14	0.05	0.296	0.13	0.04
$\langle 110 \rangle, T-Tr-T$	0.016	0.09	0.03	0.070	0.18	0.06	0.116	0.15	0.05
$\langle 111 \rangle, T-T$	0.672	0.15	0.05	1.630	0.28	0.09	3.262	0.17	0.06
$\langle 110 \rangle, O-O$	0.627	0.35	0.12	1.468	0.21	0.07	2.966	0.26	0.09
$\langle 111 \rangle, O-O$	0.195	0.13	0.05	0.713	0.25	0.08	1.083	0.19	0.06

TABLE IV: Minimal ($H_{\min}$) and maximal ($H_{\max}$) heights of the barriers between equivalent adjacent sites in the bcc lattice along various directions (see Fig.10) for K (representative of alkali metals) and Ba. Estimates of the zero-point energies of muons and protons are given. All energies are in eV.

One can also estimate the effects of lattice vibrations at $T=0$ K. The Fourier transform of the second term in the r.h.s. of Eq. IV.1 is

$$\sum_{\vec{\ell}} \int d\vec{r} \Delta n(\vec{r}-\vec{R}_\mu) W(\vec{r}-\vec{R}_\ell) = (2\pi)^{-3} \int d\vec{q} e^{i\vec{q} \cdot \vec{R}_\mu} \Delta n(q) W(q) \sum_{\vec{\ell}} e^{-i\vec{q} \cdot \vec{R}_\ell(t)} \quad (V.2)$$

where

$$\vec{R}_\ell(t) = \vec{R}_\ell^0 + \vec{u}_\ell(t), \quad (V.3)$$

with the condition

$$\langle \vec{u}(t) \rangle = 0. \quad (V.4)$$

Since we are interested only in an order of magnitude of the effect of $\vec{u}_\ell(t)$, we used the Debye-Waller approximation for the time-dependent exponential

$$\langle e^{-i\vec{q} \cdot \vec{u}(t)} \rangle = e^{-q^2 \langle u^2 \rangle / 6}. \quad (V.5)$$

Thus, the net effect of zero-point lattice vibrations is to screen the pseudopotential by a factor $e^{-q^2 \langle u^2 \rangle / 6}$. In the Debye approximation, for $T = 0$ K

$$\langle u^2 \rangle = \frac{9}{4} \frac{\hbar^2}{m k_B \theta_D} \langle m^2 \rangle = \frac{64.546}{\Lambda \theta_D} \langle a_B^2 \rangle. \quad (V.6)$$

Λ is the atomic number of the ion and θ_D the Debye temperature. The product $\Lambda \theta_D$ being always very large, we are left with small numbers for $\langle u^2 \rangle$ ($0.14 a_B^2$ for Li, $0.07 a_B^2$ for Cs), and the effect of this additional screening is small. As a result, the potential barriers are lowered or raised by amounts which are never larger than 0.007 eV. Energies of this order of magnitude are much smaller than the barriers themselves, and out of proportion with the precision expected from calculations in first order perturbation theory. We therefore neglect this contribution in the following.

Fig. 11 shows with more detail the O-T barrier in K. Curves corresponding to five pseudopotentials are shown, the crosses indicate in each case the effect of the zero-point energy of the lattice ions, and the dotted line is the structural part of the energy.

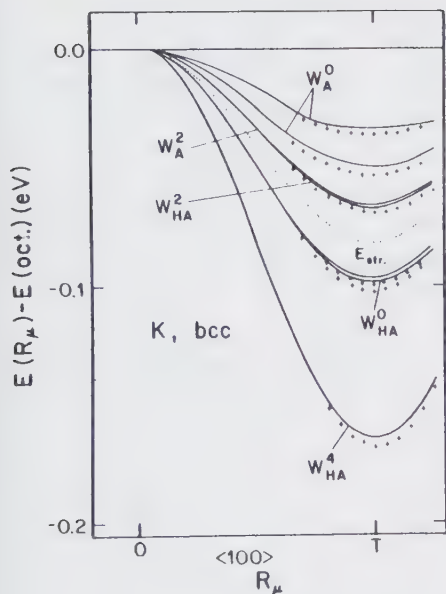


Fig 11. Detailed picture of the energy profile for a muon or a proton moving along a straight line from the T- to the O-site in K. The dotted line shows the structural part of the energy. The crosses below each curve indicate how the potentials are modified when the zero-point lattice vibrations are taken into account.

2. fcc metals

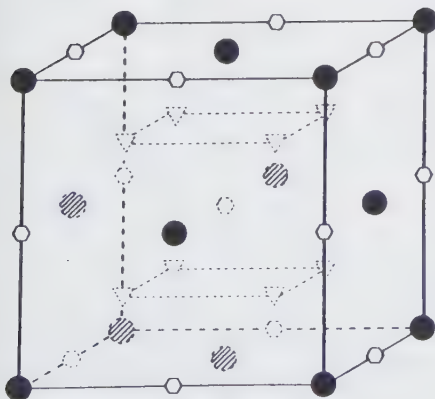


Fig. 12. fcc lattice containing octahedral (hexagons) and tetrahedral (triangles) sites.

The fcc lattice and all octahedral (hexagons) and tetrahedral (triangles) sites are shown in Fig. 12. The sites of interest for an interstitial impurity lie along the following directions:

- 1) $\langle 1\ 0\ 0 \rangle$: T-T, with distance $d = a/2$ between two adjacent T-sites,
- 2) $\langle 1\ 1\ 1 \rangle$: T-O-T, along the body-diagonal of the cube, both T-sites being at the distance $d = \sqrt{3} a/2$,
- 3) $\langle 1\ 1\ 0 \rangle$: O-O, with $d = \sqrt{2} a/2$.

We calculated the energy profiles along these directions using all the pseudopotentials of Table V (see next page). Fig.13 shows the profiles obtained in the case of Al.

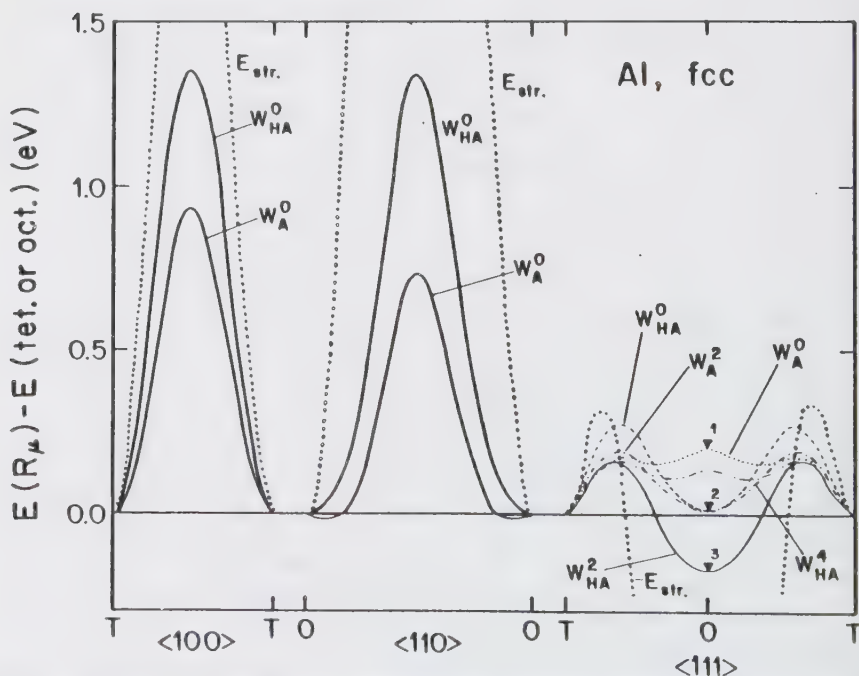


Fig. 13. Potentials seen by an impurity along various directions in Al. Along the $\langle 1\ 0\ 0 \rangle$ and $\langle 1\ 1\ 0 \rangle$ directions, only the highest and lowest barriers are plotted. In the case of the $\langle 1\ 1\ 1 \rangle$ direction, five curves are shown, and the triangles indicate the results obtained by other authors: 1 corresponds to ref 21, 2 to ref 20, and 3 to ref 18.

Metal	Z	r _s	a	W_A^0	W_A^2	W_{HA}^0	W_{HA}^2	W_{HA}^4	W_{BG}^0 (r ₁ = 1)
				ref 52 53 55 56 58	ref 60	ref 19 62 67 68	ref 59	ref 66	ref 50 51
				r _c	r _c	r _c λ	r _c λ	r _c λ	r ₂ λ v _o
Cu	1	2.664	6.831	0.813		2.42 1.125			1.815 0.50 1.90
Ag	1	3.023	7.721	1.039		2.73 1.160			2.38 0.68 2.95
Au	1	3.005	7.708	0.813		2.72 1.398			2.60 0.50 2.66
Ca	2	3.269	10.548	1.905					
Sr	2	3.554	11.499	2.13					
Al	3	2.072	7.653	1.115 1.131	1.09	1.388 0.397 1.394 0.389 2.200 1.188 2.200 1.159	1.23 0.398	1.247 0.350 1.247 0.361 1.269 0.332 1.273 0.542 2.451 1.211	
Pb	4	2.304	9.356	1.077 1.12 1.474		2.40 1.020			

TABLE V. Pseudopotential parameters for the simple metals crystallizing in the fcc structure with reference to the authors who determined them. The table also contains the jellium parameter r_s , the valence Z and the lattice constant a. All quantities are in a.u. .

In Fig.13, for the $\langle 1\ 0\ 0 \rangle$ and $\langle 1\ 1\ 0 \rangle$ directions, we show only the highest and lowest barriers as well as the structural part of the energy (Eq.IV.9, dotted line).

Along the $\langle 111 \rangle$ direction, the results corresponding to various choices for the pseudopotential differ from each other, and five typical curves are drawn. The results for this T-O-T barrier obtained by other authors are also shown and fit rather well with our own calculations.

The problem of deciding whether a proton prefers to sit at the O- or at the T-site in Al can obviously not be solved within the present model, since the results depend too strongly on the pseudopotential. However, it seems probable that a muon will see no significant potential barrier along the $\langle 111 \rangle$ direction from O- to T- site, no matter what pseudopotential is used to determine its diffusion properties.

In contrast to the bcc case, the structural part of the energy always differs from the full energy by an order of magnitude. As mentioned in Sec.IV.1, this is related to the small r_s -values characterizing fcc (and hcp) metals. It should also be noticed that the highest barriers coincide now with w_{HA}^O and not with the most screened pseudopotential w_{HA}^4 as in the bcc case. However, the smallest barriers are still those calculated using w_A^O .

The situation in other fcc metals differs from one element to the other.

- a) In Pb, all three pseudopotentials (see Table V) lead to very different results as concerning the site of lowest energy. However, the barrier heights are always quite small at least in one of the three directions studied: w_A^O (with $r_c=1.474$) gives the lowest barrier along the $\langle 100 \rangle$ direction, w_A^O (with $r_c=1.077$) along the $\langle 110 \rangle$ direction, and w_{HA}^O along the $\langle 111 \rangle$ direction. Thus, neither a proton nor a muon is expected to be localized in Pb.
- b) Different is the situation in Ca and Sr. The bare Ashcroft pseudopotential (which in all previous cases predicted the lowest potential barriers as compared to other pseudopotentials) predicts a strong localization for both muons

and protons at the T-site (see Table VI).

	Direction	H	$E_O(\mu^+)$	$E_O(p^+)$
Sr	$\langle 1\ 0\ 0 \rangle$, T-T	0.84	0.34	0.11
	$\langle 1\ 1\ 1 \rangle$, T-O-T	1.17	0.24	0.08
Ca	$\langle 1\ 0\ 0 \rangle$, T-T	0.93	0.37	0.12
	$\langle 1\ 1\ 1 \rangle$, T-O-T	1.02	0.24	0.08

TABLE VI. Height H of the potential barriers along the $\langle 1\ 0\ 0 \rangle$ (T-T) and the $\langle 1\ 1\ 1 \rangle$ (T-O-T) directions in Sr and Ca. The zero-point energies of a muon and a proton are indicated. Both a μ^+ and a p^+ seem to be strongly localized at the T-site. All energies are in eV.

c) The potentials along all directions are shown in Fig.14 for the case of noble metals, using the bare Heine-Abarenkov pseudopotential (called "Nikulin pseudopotential" by some authors in the case of noble metals).

In the $\langle 1\ 0\ 0 \rangle$ direction (T-T), the height of the potential barrier decreases rapidly as one goes from Cu to Au. This is even more pronounced along the $\langle 1\ 1\ 0 \rangle$ direction (O-O). The difference is still more marked along the $\langle 1\ 1\ 1 \rangle$ direction (T-O-T): in Cu, the O-site has lowest energy ($E_O - E_T = -0.6$ eV: Teichler^{70,71} predicted some -0.8 eV) where a proton and even a muon could be localized. In Ag, a proton could still be localized at the O-site, whereas more detailed calculations are needed in order to determine whether a muon could be localized or not. In Au, the minimum along the T-O-T direction corresponds to the T-site, with $E_O - E_T = 0.48$ eV. Further, the lowest barrier is along the $\langle 1\ 0\ 0 \rangle$ direction between two T-sites.

The pseudopotential of Borchì and De Gennaro w_{BG}^O predicts

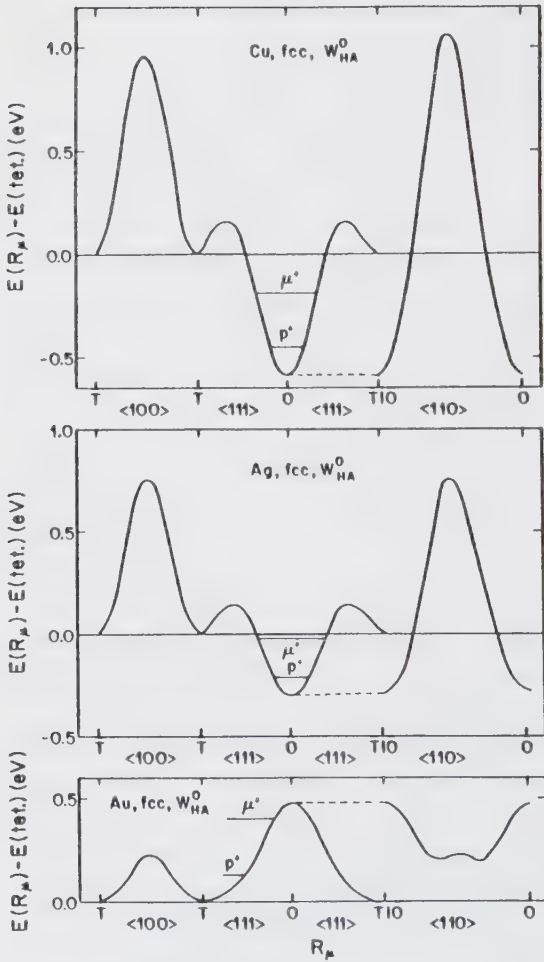


Fig. 14. Energy profiles in noble metals obtained with W_{HA}^0 . The zero-point energies of a muon and a proton are indicated. The potentials are similar to those predicted by W_{BG}^0 (see Table V) in the cases of Cu and Ag, but not in Au, where W_{BG}^0 predicts a deep well (-0.85 eV) at the O-site.

also a strong localization of muons and protons in Cu ($E_O - E_T = -1.6$ eV), a less strong localization in Ag ($E_O - E_T = -0.3$ eV), but again a strong localization in Au ($E_O - E_T = -0.85$ eV). These results are in contradiction with those obtained from the bare Ashcroft pseudopotential W_A^0 which predicts in general much smaller barriers and wells, preventing any localization.

3. hcp metals

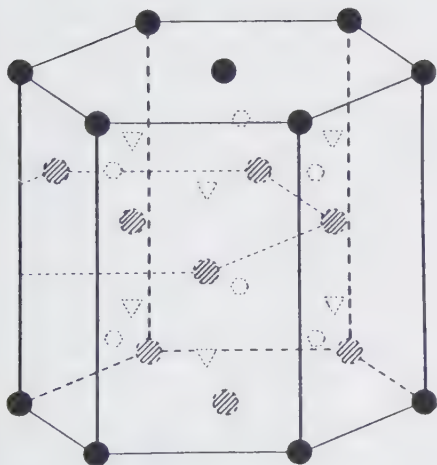


Fig. 15. hcp lattice with its octahedral (hexagons) and tetrahedral (triangles) sites.

The hcp structure with its O- and T-sites is shown in Fig.15. The O-sites lie in the $z = \frac{1}{4}c$ and $z = \frac{3}{4}c$ planes, while the T-sites lie in slightly displaced planes (this being due to the presence of an ion nearby in the $z = \frac{1}{2}c$ plane). Thus, in the c -direction, the sequence for symmetric sites is the following:

O-O-O- ... or
T-ion-T-T-ion-T-

The sites of interest lie along the following directions:

- 1) $\langle 0 0 1 \rangle$: O-O, with distance $d = c/2$ between two neighboring O-sites,
- 2) $\langle 1 1 0 \rangle$: O-O, with $d = a$, in the $z = \frac{1}{4}c$ plane,
- 3) $\langle 1 0 \sim 0 \rangle$: O-T, with $d_{OT} = \frac{a}{3} \sqrt{3 + a^2/c^2}$, when going from an O-site to the nearest T-site,
- 4) $\langle 0 0 1 \rangle$: T-T, with $d = (\frac{1}{2} \frac{c}{a} - \frac{2}{3} \frac{a}{c}) a$.

In the $\langle 1 1 0 \rangle$ direction joining two T-sites lying in the same plane (with $d = a$), a high barrier always exists ($2.3 < H < 4.9$ eV) for all elements and all pseudopotentials (see Table VII).

The energy profiles in Mg are shown in Fig. 16 for two pseudopotentials. The structural part of the energy (dotted line) differs, as for fcc metals, by an order of magnitude from the

from the full energy $E(\vec{R}_\mu)$. The results published by Popovic and Stott¹⁹ are represented by triangles. The curves indicate a slight minimum at the T-sites, which is too shallow however to localize a muon or even a proton.

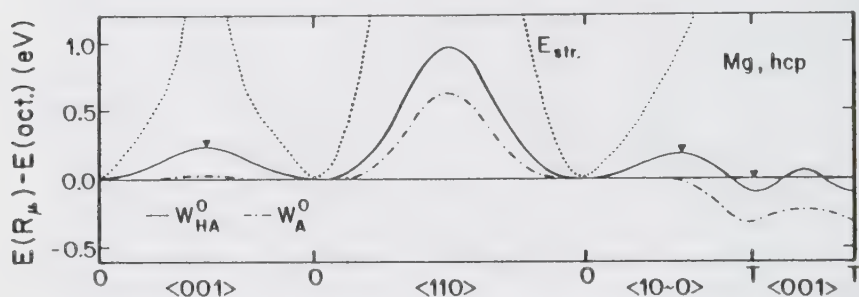


Fig. 16. Potentials obtained with W_A^O (dotted-dashed line) and W_{HA}^O (full line) in Mg along various directions. The triangles show the results obtained by Popovic and Stott¹⁹ using W_{HA}^O .

Element r_s	Z a	c/a	W_A^O , ref. {52,53,56} r_c	W_{HA}^O , ref. {19} r_c λ
Be 1.874	2 4.318	1.567	1.055	
Mg 2.642	2 6.064	1.624	1.358 1.39	1.69 0.451
Zn 2.304	2 5.025	1.856	1.11 1.272	
Cd 2.590	2 5.629	1.886	1.247	

TABLE VII. Pseudopotential parameters for the simple metals crystallizing in the hcp structure, with reference to the authors who determined them. The table also contains the jellium parameter r_s , the valence and the lattice constant. All quantities are in atomic units.

In Zn, the barriers between O-sites are quite high (0.8 eV along the $\langle 0\ 0\ 1 \rangle$ direction and 1.11 eV along the $\langle 1\ 1\ 0 \rangle$ direction), as well as the T-T- barrier along the $\langle 0\ 0\ 1 \rangle$ direction (0.42 eV). The lowest barrier corresponds to the O-T jump (0.36 eV) with a very shallow minimum at the T-site ($E_O - E_T \approx -0.1$ eV). Because of the short distance between nearest O- and T- sites, this is not sufficient to localize a muon.

For Cd, all barriers are extremely flat. As in the cases of Mg and Zn, the tetrahedral site has lowest energy ($E_O - E_T \approx 0.3$ eV).

The situation is different in the case of Be, where all barriers are very high, and where the T-site has a much larger energy than the O-site ($E_T - E_O \approx 0.7$ eV). The heights of the barriers as well as the zero-point energies of muons and protons are given in Table VII. The calculations predict that both protons and muons are strongly localized at O-sites in Be. There is some experimental evidence for muons being localized in Be⁷².

Direction	H	$E_O (\mu^+)$	$E_O (p^+)$
$\langle 0\ 0\ 1 \rangle$, O-O	1.27	0.70	0.24
$\langle 1\ 1\ 0 \rangle$, O-O	3.25	0.80	0.27
$\langle 1\ 0\ 0 \rangle$, O-T	1.18	0.73	0.24

TABLE VIII. Heights H of the potential barriers along the $\langle 0\ 0\ 1 \rangle$, $\langle 1\ 1\ 0 \rangle$ and $\langle 1\ 0\ 0 \rangle$ directions in Be and estimates of the zero-point energies of muons and protons in these potentials. Both particles might well be localized at the O-site in Be. All energies are in eV.

VI. QUALITATIVE STUDY OF OTHER EFFECTS

1. Lattice relaxation in Al and Cs

We calculated the effect of lattice expansion or contraction of the first two shells in the cases of Al and Cs. We supposed that the lattice ions are displaced around a given interstitial site $\vec{R}_s = \vec{R}_{\text{oct}}$ or $\vec{R}_{\text{tet}}$ in the radial direction:

$$(\vec{R}_s - \vec{R}_\ell) \rightarrow (1 + \delta_i)(\vec{R}_s - \vec{R}_\ell), \quad (\text{VI.1})$$

where i numbers the shells. We fixed the displacement of the second shell to be

$$\delta_2 = \pm 0.2 \delta_1. \quad (\text{VI.2})$$

If $E^O(\vec{R}_\mu)$ is the energy of the unperturbed lattice and $E^{\text{rel}}(\vec{R}_\mu)$ the energy of the relaxed one, the change is

$$E^{\text{rel}}(\vec{R}_\mu) - E^O(\vec{R}_\mu) = \sum_{\ell} \{E(X_\ell^{\text{rel}}) - E(X_\ell^O)\}, \quad (\text{VI.3})$$

where the sum goes over the ions which are relaxed. X_ℓ^O and X_ℓ^{rel} are defined as

$$X_\ell^O = |\vec{R}_\mu - \vec{R}_\ell|, \quad (\text{VI.4})$$

and

$$X_\ell^{\text{rel}} = |\vec{R}_\mu - \vec{R}_\ell + \delta_i(\vec{R}_s - \vec{R}_\ell)|. \quad (\text{VI.5})$$

The function $E(X)$ is the energy of the impurity at distance X from one single ion, and has been calculated in Appendix D (see Eq. D.11).

For Al, the resulting change in energy is shown in Fig.17 (for $\vec{R}_s = \vec{R}_{\text{oct}}$ and $\delta_2 = -0.2 \delta_1$, see next page), and in Fig.18 (for $\vec{R}_s = \vec{R}_{\text{tet}}$ and $\delta_2 = +0.2 \delta_1$, see page 56). In both cases, δ_1 was varied from -0.06 up to +0.06. The value of δ_1 is indicated on each curve.

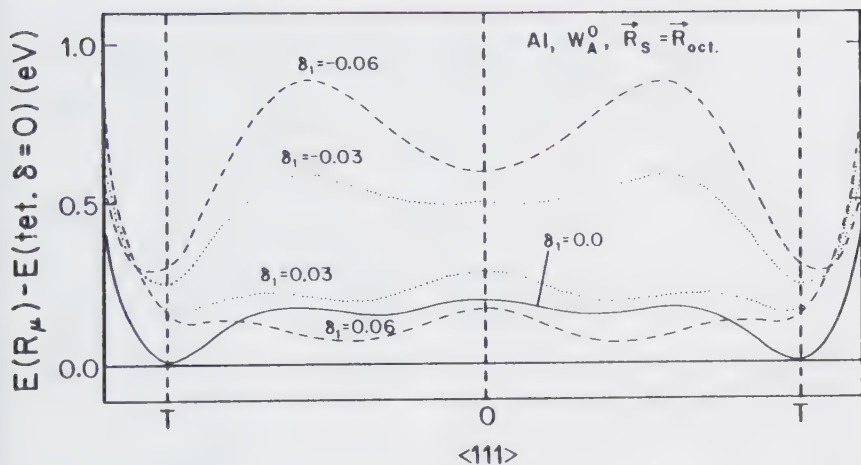


Fig. 17. Effect on the energy profile (along the $\langle 111 \rangle$ direction in Al) when the lattice is relaxed about the O-site. The first shell is relaxed in the radial direction by $\delta_1 = -6\%$ up to $\delta_1 = +6\%$, and the second shell by $\delta = -0.2\delta_1$. The value of δ_1 is indicated on each curve. The full line ($\delta_1 = 0$.) corresponds to the rigid lattice.

Both Figs.17 and 18 have been calculated using the bare Ashcroft pseudopotential W_A^0 with $r_c = 1.115$.

As is seen from Fig.17, even a large expansion or contraction about the O-site does not render it more stable. Further, the effect of this relaxation modifies considerably the energy at the neighboring T-sites.

On the other hand, Fig.18 shows that the situation is different if the lattice is relaxed about the T-site: an expansion of the first shell together with an expansion of the second shell lowers the energy at the T-site without perturbing significantly the energy at the O-site.

It should be mentioned that the influence of the second shell is quite small (of the order of 0.01 eV) in Al, as has been

checked by changing the sign of δ_1/δ_2 in both cases.

Perrot and Rasolt⁶⁰ have calculated anisotropic lattice relaxation effects in Al, using w_A^2 and w_{HA}^2 (see Table V). They found a relaxation energy of -0.06 eV corresponding to $\delta_1 = 2$ to 3 % in magnitude.

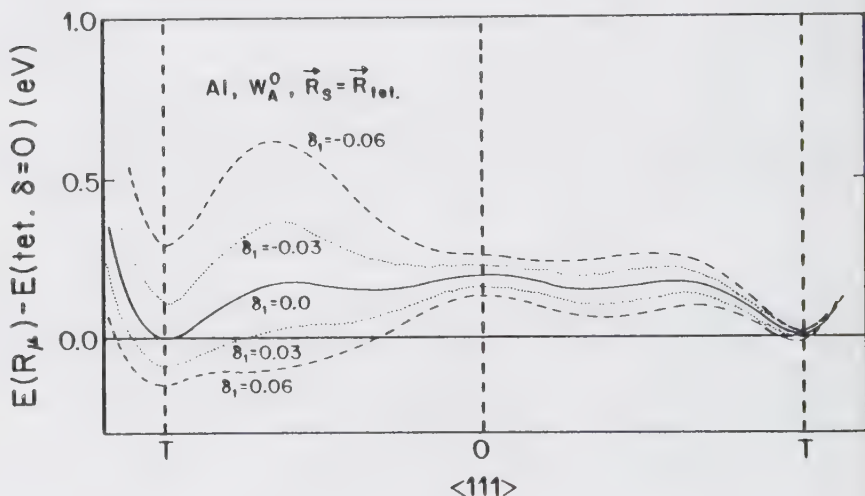


Fig. 18. Effect on the energy profile (along the $\langle 111 \rangle$ direction in Al) when the lattice is relaxed about the T-site. The first shell is relaxed in the radial direction by $\delta_1 = -6\%$ up to $\delta_1 = +6\%$, and the second shell by $\delta_2 = 0.2\delta_1$. The value of δ_1 is indicated on each curve. The full line ($\delta_1 = 0$) corresponds to the rigid lattice.

In the case of Cs, we relaxed the lattice around the T-site (by $\delta_1 = -0.06$ up to $+0.06$) and calculated the energy profile in both the $\langle 100 \rangle$ (T-O-T) and $\langle 110 \rangle$ (T-Tr-T) directions. As in the case of Al, the relaxation of the second shell does not influence significantly the energy profiles, which are shown in Fig. 19 (with $\delta_2 = -0.2\delta_1$). A contraction of the first shell

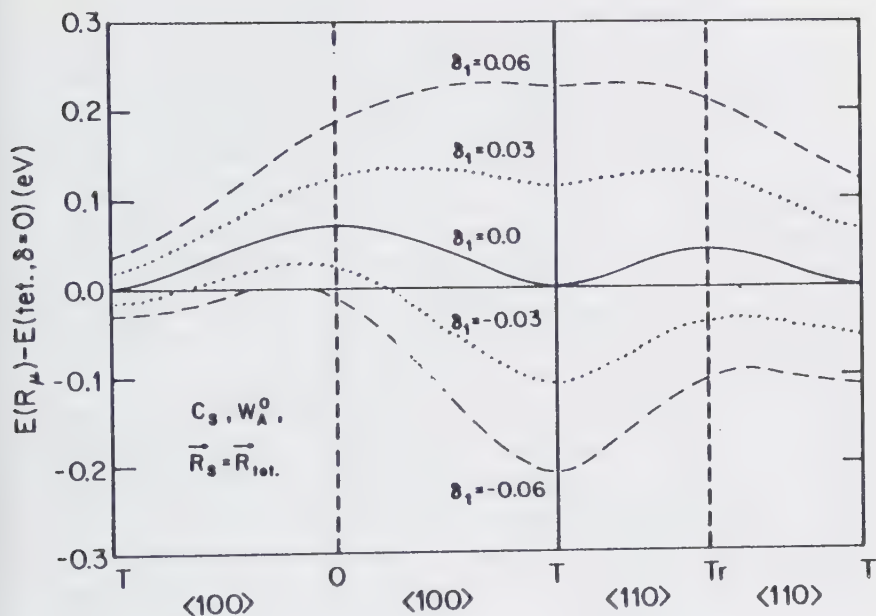


Fig. 19. Effect on the energy profile (along the $\langle 1\ 0\ 0 \rangle$ (T-O-T) and $\langle 1\ 1\ 0 \rangle$ (T-Tr-T) directions in Cs) when the lattice is relaxed about the T-site by $\delta_1 = -6\%$ up to $\delta_1 = +6\%$ for the first shell, and by $\delta_2 = -0.2\delta_1$ for the second shell. The value of δ_1 is indicated on each curve. The full line ($\delta_1 = 0$) corresponds to the rigid lattice.

lowers the energy at the T-site by a considerable amount. This could be due to the much larger oscillations of the perturbed charge density in Cs than in Al (see Fig.3).

Although these results are only qualitative, they show that lattice relaxation (at least of the first shell) modifies the energy profiles. In addition, the effect has to be calculated separately for each element, since it is sometimes an expansion (Al, T-site, Fig.18) and sometimes a contraction (Cs, Fig.19)

which lowers the energy.

2. Effect of a substitutional impurity in Al

Since no crystal can be found in a 100 % pure state, the question of the influence of defects on the behavior of light interstitials in solids is of major importance. The influence on muons of vacancies and substitutional impurities has been studied by a number of experimental groups. Theoretically, the treatment of vacancies requires the recalculation of the perturbed charge density (see Eq. I.2). Therefore, we investigated only the influence of substitutional impurities in Al, where the experimental situation can be summarized as follows: in high purity, undamaged Al, muons are observed not to depolarize over the temperature range 0.03 to 300 K^{73,74,75,76} implying either fast diffusion or delocalization of the muon wave function.

However, a small admixture of some substitutional impurities produces trapping of muons, as observed by a number of groups. This is the case in particular for Al(Cu), Al(Li), Al(Zn), Al(Mg) or Al(Ag)⁷³⁻⁸³. In general, the initial trapping is random, and regions close to the impurity are reached only by diffusion⁸⁴. Further, one observes a stronger trapping for increased impurity density⁷³.

Within the present model, we can easily simulate a substitutional impurity by removing one host ion and replacing it by a substitutional impurity. This is straightforward when using Eq.(D.11) (see Appendix D). However, this procedure implies an additional approximation: the electron distribution is modified around the substitutional impurity (in particular when the valence of the host is different from that of the impurity). This has not been taken into account. However, as discussed in Sec. IV.2, the use of pseudopotentials renders our approximation reasonable. Additionally, lattice relaxation around substitutional

impurities could well be large, and calculations of the total heat of solution are necessary to determine with precision the local geometry of the perturbed system.

Therefore, the results contained in this section are to be considered as qualitative.

We calculated the change in energy ΔE experienced by a muon at various interstitial sites in Al, produced by the presence of a substitutional impurity situated on one of the first four shells around the muon. All ions were simulated by an Ashcroft empty-core pseudopotential w_A^O , and ΔE was determined as a function of the core radius r_C of the substitutional impurity and of its valence Z_I .

The change in energy for a muon at the T-site is shown in Fig.20. Three curves (for $Z_I = 1, 2$ or 3) correspond to a substitutional impurity with core radius r_C , located on the first shell around the T-site (R_1), and two curves (for $Z_I = 1$ or 3) for the impurity on the second shell (R_2).

The change in energy for impurities located further away from the muon is too small ($\sim$ meV) to be shown at the same scale. This indicates that, within our model, a muon does not feel a substitutional impurity, except in its immediate neighborhood.

As can be seen on Fig.20, the substitutional impurity has the effect of a repulsive potential if its core radius is large. Further, the larger Z_I , the larger the repulsion. On the other hand, for $Z_I < Z_h$ (valence of the host) and small r_C , the substitutional impurity acts as a trapping center.

Fig.21 (p. 61) shows the energy profile in Al along the $\langle 111 \rangle$ direction (T-O-T): a Cu-ion ($r_C = 0.81$, see Fig.20) is located at the origin (0,0,0) in an otherwise pure Al host. As the position $\vec{R}_\mu$ of the muon is varied along the $\langle 111 \rangle$ direction, the muon first reaches the nearest T-site (1/4,1/4,1/4), then an O-site (1/2,1/2,1/2) and finally another T-site (3/4,3/4,3/4). The potential of the muon in the pure host is shown by a full line, and the change induced by the Cu-ion by a dotted line.

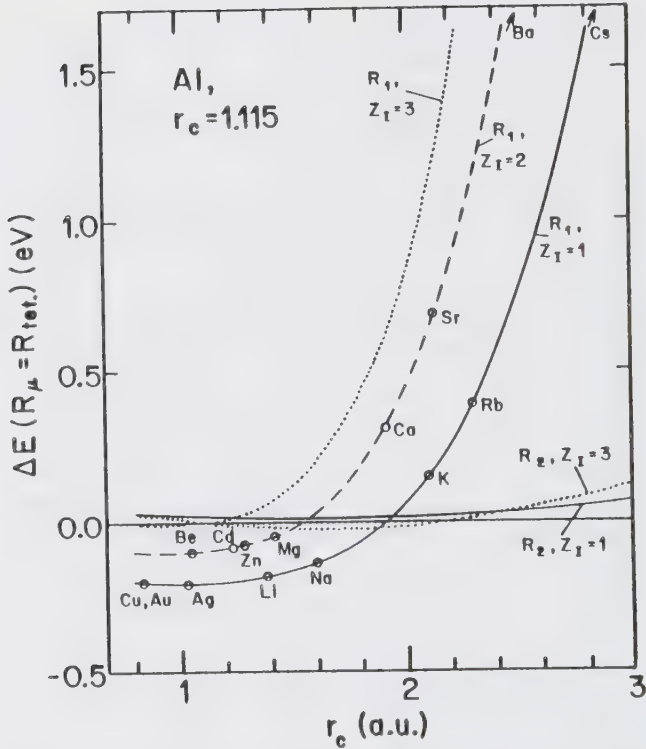


Fig. 20. Change in energy for a muon or a proton at the tetrahedral site in Al if a substitutional impurity (with valence $Z_I=1,2$ or 3) replaces an Al ion on the first shell (R_1) or on the second shell (R_2). All ions are simulated by an Ashcroft empty-core pseudopotential W_A^0 , and the lattice is unrelaxed. Substitutional impurities with small valence (with respect to that of the host) and small core radii attract the muon or the proton.

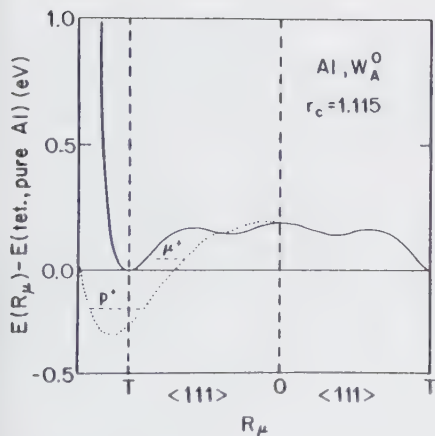


Fig. 21. Comparison between the energy profile along the $\langle 111 \rangle$ direction in pure Al (full line) and in Al doped with Cu. A Cu ion sitting at $(0,0,0)$ could trap a proton (or a muon) close to the nearest T-site $(1/4, 1/4, 1/4)$.

An estimate of the zero-point energy of muons and protons in the perturbed potential is also shown. The minimum of the energy is slightly displaced towards the Cu-ion, and is deep enough to trap a p^+ . Since lattice relaxation effects (not included in the present calculation) are still able to lower the energy by some additional 0.1 to 0.2 eV (see Fig.18), it seems highly probable that a muon would be trapped close to the T-site.

In the case of a muon at the O-site, curves very similar to Fig.20 can be obtained, the attractive region, however, being shallower.

VII. SUMMARY AND CONCLUSIONS

Using the self-consistent density functional formalism, the electron density around a unit positive charge in jellium has been calculated and parametrized for $2.0 < r_s < 6.0$. These results have then been used to compute energy profiles in 17 simple metals using many different local pseudopotentials in first order perturbation theory. The dependence of the energies on the choice of pseudopotential, which in some cases is strong, exhibits the relative weakness of this approach. Nevertheless, a good physical insight can be gained on the behavior of hydrogen-like interstitials in most simple metals: within our model, the results for different pseudopotentials differ in most cases by less than 20%. In addition, the sites of lowest energy and the easiest diffusion paths can be predicted for many metals. The question whether the impurity can be localized or not has been investigated.

Hydrogen diffusion experiments⁸⁵ show a much smaller activation energy in bcc metals than in fcc or hcp lattices. We observed the same trend in our calculations. In alkali metals with bcc structure, the barriers along the $\langle 1\ 0\ 0 \rangle$ (T-O-T) as well as along the $\langle 1\ 1\ 0 \rangle$ (T-Tr-T) directions never exceed 0.2 eV, favoring an easy diffusion of light impurities. In bcc Ba (with $Z = 2$), only a proton or one of its heavier isotopes could be localized at the T-site.

The situation is different in fcc and hcp simple metals: in Al and Pb, muons and protons see almost no barrier along the body-diagonal of the cube ($\langle 1\ 1\ 1 \rangle$, T-O-T direction). However, a strong localization at the T-site is predicted for both Ca and Sr. In Cu, two pseudopotentials predict a localization of muons and protons at the O-site, and all our calculations indicate a much weaker localization in Ag. For Au, the results obtained using various pseudopotentials are in contradiction. μ SR experiments^{78,86} in Cu show a localization of muons below 100 K at the octahedral site. Blocking experiments on the localization

of pions⁸⁷ in Au are in preparation. The muon diffusion rate at high temperatures⁸⁸ decreases when going from Au to Ag to Cu.

In hcp Mg, Zn, and Cd no high barriers are present, whereas light interstitials may easily be trapped at the O-sites in Ba.

Since a small lattice relaxation ($< 3\%$ in magnitude) does not too strongly affect these results, a more detailed study seems necessary only in the cases where the zero-point energy of the impurity is of the same order of magnitude as the barrier heights. A full treatment of lattice relaxation and of the zero-point motion (including the calculation of the impurity wave-function in the anharmonic three-dimensional potential) is then needed to give reliable results. This is the case in Au, Al, Pb and Zn.

μ SR experiments using Al samples doped with Cu, Ag, Li, Zn or Mg can be qualitatively explained: in many cases, trapping of muons in the immediate vicinity of these ions is probable. This implies a stronger trapping rate for increased impurity density. On the other hand, however, substitutional impurities in Al having a large core radius act as a repulsive potential on the muon. More general investigations about these effects in other simple metals are in preparation.

APPENDIX A: RICCATI-BESSEL FUNCTIONS

The Riccati-Bessel functions of the first kind $\hat{j}_\ell(z)$ and of the second kind $\hat{n}_\ell(z)$ are solutions of the Riccati-Bessel equation

$$\hat{f}_\ell''(z) + \left\{1 - \frac{\ell(\ell+1)}{z^2}\right\} \hat{f}_\ell(z) = 0. \quad (\text{A.1})$$

They are related to the spherical Bessel functions of the first and second kind by

$$\hat{f}_\ell(z) = z f_\ell(z), \quad f = j, n. \quad (\text{A.2})$$

Parity

$$\hat{j}_\ell(-z) = (-1)^{\ell+1} \hat{j}_\ell(z), \quad \hat{n}_\ell(-z) = (-1)^\ell \hat{n}_\ell(z). \quad (\text{A.3})$$

Asymptotic behavior

$$\hat{j}_\ell(z \rightarrow \infty) = \sin(z - \ell\frac{\pi}{2}), \quad \hat{n}_\ell(z \rightarrow \infty) = -\cos(z - \ell\frac{\pi}{2}). \quad (\text{A.4})$$

Expansion for small arguments

$$\begin{aligned} \hat{j}_\ell(z \rightarrow 0) &= \frac{z^{\ell+1}}{(2\ell+1)!!!} \left\{ 1 - \frac{z^2/2}{1!(2\ell+3)} + \frac{(z^2/2)^2}{2!(2\ell+3)(2\ell+5)} - \dots \right\} \\ \hat{n}_\ell(z \rightarrow 0) &= -\frac{(2\ell-1)!!!}{z^\ell} \left\{ 1 - \frac{z^2/2}{1!(2\ell-1)} + \frac{(z^2/2)^2}{2!(2\ell-1)(2\ell-3)} - \dots \right\} \end{aligned} \quad (\text{A.5})$$

First functions

$$\begin{aligned} \hat{j}_0(z) &= \sin(z) & \hat{n}_0(z) &= -\cos(z) \\ \hat{j}_1(z) &= \frac{1}{z} \sin(z) - \cos(z) & \hat{n}_1(z) &= -\frac{1}{z} \cos(z) - \sin(z) \end{aligned} \quad (\text{A.6})$$

$$(\text{A.7})$$

Recurrence formula

$$\hat{f}_{\ell+1}(z) = -\hat{f}_{\ell-1}(z) + \frac{2\ell+1}{z} \hat{f}_\ell(z), \quad (\text{A.8})$$

with $\hat{f}_\ell = \hat{j}_\ell, \hat{n}_\ell$.

APPENDIX B: NUMEROV METHOD⁴⁰

Numerov method is a very fast, easy and precise way of solving numerically second order differential equations of the type

$$f''(r) = g(r)f(r) . \quad (B.1)$$

The method starts with the Taylor expansion

$$f(r \pm h) = f(r) \pm hf'(r) + \frac{1}{2} h^2 f''(r) \pm \dots \quad (B.2)$$

The second derivative of (B.2) is:

$$f''(r \pm h) = f''(r) \pm hf'''(r) + \frac{1}{2} h^2 f''''(r) \pm \dots \quad (B.3)$$

If one defines

$$y(r) = f(r) - \frac{h^2}{12} f''(r) , \quad (B.4)$$

one can see from Eqs. (B.2) and (B.3) that

$$y(r+h) + y(r-h) = 2 f(r) + \frac{5}{6} h^2 f''(r) + O(h^6) . \quad (B.5)$$

The sixth and higher orders in h are neglected.

Using Eqs. (B.5), (B.4) and finally (B.1) one obtains

$$y(r+h) - 2 y(r) + y(r-h) = h^2 f''(r) = h^2 g(r) f(r) . \quad (B.6)$$

Using Eqs. (B.4) and (B.1), Eq. (B.6) is easily transformed into

$$y(r+h) = 12 x(r) y(r) + 2y(r) - y(r-h) , \quad (B.7)$$

where the known function $x(r)$ is defined by

$$x(r) = \frac{h^2 g(r)/12}{1 - h^2 g(r)/12} . \quad (B.8)$$

Eq. (B.7) gives finally the recurrence formula for y :

$$y(r+h) = 2\{1+6 x(r)\} y(r) - y(r-h) . \quad (B.9)$$

Thus, if $y_0 = y(r_0)$ and $y_1 = y(r_0+h)$ are given, the function $y(r)$ can be easily determined from (B.9) and (B.8). Then, $f(r)$ is obtained through Eqs. (B.4) and (B.1):

$$f(r) = \frac{y(r)}{1-h^2 g(r)/12} . \quad (B.10)$$

The application of the Numerov method to solving the radial part of the Schrödinger equation (III.7) is straightforward. With the boundary condition (III.8), one has $f(r=0) = 0$ and $f(r=h) = h^{\ell+1}$ (the normalisation constant has been set equal to 1). Using Eq. (B.10), this gives $y_0 = 0$ and $y_1 = h^{\ell+1} \{1-h^2 g(h)/12\}$, where $g(r)$ stands for

$$g(r) = \frac{\ell(\ell+1)}{r^2} + 2 V_{\text{eff}}(r) - 2E . \quad (B.11)$$

E is $k^2/2$ for scattering states, and E_{1s} for bound states, with $\ell = 0$.

APPENDIX C: ASYMPTOTIC BEHAVIOR OF THE DENSITY

The asymptotic behavior of the perturbed charge density $\Delta n(r)$ around a point charge in an electron gas can be determined analytically. The impurity produces a spherically symmetric potential $V(r)$, and the perturbed wave functions are characterized by phase shifts $\delta_\ell(k)$. In the unperturbed case (homogeneous electron gas), the potential $V(r)$ is of course zero, as well as the phase shifts. We denote therefore with an upper index 0 the quantities corresponding to the unperturbed electron gas. By definition, the perturbed charge density is

$$\begin{aligned}\Delta n(r) &= n(r) - n_0 \\ &= 2 \frac{V}{8\pi} \int d\vec{k} \{ |\psi_{\vec{k}}(\vec{r})|^2 + |\psi_{\vec{k}}^0(\vec{r})|^2 \} \theta(k_F - k). \quad (C.1)\end{aligned}$$

Using the decomposition (III.6) for $\psi_{\vec{k}}$, Eq. C.1 is reduced to

$$\Delta n(r) = \frac{V}{2\pi^2} \sum_{\ell} (2\ell+1) \int_0^{k_F} dk k^2 \{ u_{\vec{k},\ell}^2(r) - u_{\vec{k},\ell}^{02}(r) \}. \quad (C.2)$$

Using the asymptotic condition (III.9), the brackets in Eq. C.2 are easily transformed into

$$u_{\vec{k},\ell}^2(r \rightarrow \infty) - u_{\vec{k},\ell}^{02}(r \rightarrow \infty) = (-1)^\ell k^{-2} \sin \delta_\ell(k) \sin(2kr + \delta_\ell(k)), \quad (C.3)$$

leading to the asymptotic form for $\Delta n(r)$

$$\Delta n(r \rightarrow \infty) = \left\{ \frac{C^1}{\pi r} \right\}^2 \sum_{\ell} (-1)^\ell (2\ell+1) I_\ell(r), \quad (C.4)$$

where

$$I_\ell(r) = \int_0^{k_F} dk \sin \delta_\ell(k) \sin(2kr + \delta_\ell(k)). \quad (C.5)$$

This integral is easily split into two parts, both of which can be integrated by parts, with the result

$$I_{\ell}(r) = \frac{-1}{2r} \sin \delta_{\ell}(k) \left\{ \cos \delta_{\ell}(k) \cos(2kr) - \sin \delta_{\ell}(k) \sin(2kr) \right\} \Big|_0^{k_F} + \\ + \frac{1}{2r} \int_0^{k_F} dk \delta'_{\ell}(k) \{ \cos(2\delta_{\ell}(k)) \cos(2kr) - \\ \sin(2\delta_{\ell}(k)) \sin(2kr) \} . \quad (C.6)$$

The prime denotes the derivative with respect to the argument. With the condition

$$\delta_{\ell}(k=0) = 0, \quad (C.7)$$

Eq. C.6 is easily reduced to

$$I_{\ell}(r) = \frac{-1}{2r} \sin \delta_{\ell} \cos(2k_F r + \delta_{\ell}) + \frac{1}{2r} \int_0^{k_F} dk \delta'_{\ell}(k) \{ \cos 2\delta_{\ell}(k) \cos(2kr) - \\ - \sin 2\delta_{\ell}(k) \sin(2kr) \}, \quad (C.8)$$

where δ_{ℓ} stands for $\delta_{\ell}(k_F)$.

The first term on the r.h.s. of Eq. C.8 can now be reinserted into (C.4) and gives the leading term in the asymptotic expansion of $\Delta n(r)$

$$\Delta n(r \rightarrow \infty) = \sum_{\ell} A_{\ell} \sin \delta_{\ell} \frac{\cos(2k_F r + \delta_{\ell})}{r^3}, \quad (C.9)$$

where

$$A_{\ell} = (-1)^{\ell+1} \frac{2\ell+1}{2\pi^2}. \quad (C.10)$$

The next term of the expansion can be obtained by intergrating again by parts the remainder of Eq. C.8. The result is

$$- \sum_{\ell} \frac{1}{2} A_{\ell} \delta'_{\ell} \frac{\sin(2k_F r + 2\delta_{\ell})}{r^4} + \sum_{\ell} \frac{1}{2} A_{\ell} \frac{1}{r^4} \int_0^{k_F} dk \{ \delta''_{\ell}(k) \sin(2kr + 2\delta_{\ell}(k)) + \\ + 2\delta'_{\ell}{}^2(k) \cos(2kr + 2\delta_{\ell}(k)) \}. \quad (C.11)$$

Now, Eq. C.4 can be put in the form of Eq. III.36

$$\Delta n(r \rightarrow \infty) = A \frac{\cos(2k_F r + \phi)}{r^3} - B \frac{\sin(2k_F r + \chi)}{r^4} + O(r^{-5}) \quad (C.12)$$

if

$$A^2 = \left\{ \sum_{\ell} A_{\ell} \sin \delta_{\ell} \cos \delta_{\ell} \right\}^2 + \left\{ \sum_{\ell} A_{\ell} \sin^2 \delta_{\ell} \right\}^2, \quad (C.13)$$

$$\sin \phi = \frac{1}{A} \sum_{\ell} A_{\ell} \sin^2 \delta_{\ell}, \quad (C.14)$$

and

$$B^2 = \left\{ \sum_{\ell} \frac{1}{2} A_{\ell} \delta'_{\ell}(k=k_F) \cos 2\delta_{\ell} \right\}^2 + \left\{ \sum_{\ell} \frac{1}{2} A_{\ell} \delta'_{\ell}(k=k_F) \sin 2\delta_{\ell} \right\}^2, \quad (C.15)$$

$$\sin \chi = \frac{1}{B} \sum_{\ell} \frac{1}{2} A_{\ell} \delta'_{\ell}(k=k_F) \sin 2\delta_{\ell}. \quad (C.16)$$

In these equations, as mentioned previously, δ_{ℓ} stands for $\delta_{\ell}(k_F)$.

APPENDIX D: EVALUATION OF THE ENERGY FOR A SINGLE ION

For a single ion at $\vec{R}$, the energy (Eq. IV.1) is given by:

$$E(\vec{R}_\mu) = \frac{Z}{|\vec{R}-\vec{R}_\mu|} + \int d\vec{r} \Delta n(\vec{r}-\vec{R}_\mu) W(\vec{r}-\vec{R}) . \quad (D.1)$$

With $\vec{X} = \vec{R}-\vec{R}_\mu$ and since $\int d\vec{r} \Delta n(\vec{r}) = 1$, Eq. (D.1) reduces to

$$E(\vec{X}) = \int d\vec{s} \Delta n(\vec{s}) \left\{ \frac{Z}{X} + W(\vec{s}-\vec{X}) \right\} . \quad (D.2)$$

In the case of the Ashcroft empty-core pseudopotential

$$W(\vec{s}-\vec{X}) = - \frac{Z}{|\vec{s}-\vec{X}|} + \frac{Z}{|\vec{s}-\vec{X}|} \Theta(r_c - |\vec{s}-\vec{X}|) , \quad (D.3)$$

one can split Eq. D.2 into two parts

$$E(\vec{X}) = Z \int d\vec{s} \Delta n(\vec{s}) \left\{ \frac{1}{X} - \frac{1}{|\vec{s}-\vec{X}|} \right\} + Z \int d\vec{s} \frac{\Delta n(\vec{s})}{|\vec{s}-\vec{X}|} \quad (D.4)$$

$$= E_\infty(\vec{X}) + E_{\text{core}}(\vec{X}) . \quad (D.5)$$

Using the expansion of $1/|\vec{s}-\vec{X}|$ in Legendre polynomials and the orthonormality relation of the P_ℓ 's, E_∞ is easily transformed into

$$E_\infty(x) = \frac{Z}{X} 4\pi \int_X^\infty dr \Delta n(r) r(r-X) = \frac{Z}{X} \{F(X) - X G(X)\} , \quad (D.6)$$

where

$$F(X) = 4\pi \int_X^\infty dr r^2 \Delta n(r) , \quad (D.7)$$

and

$$G(X) = 4\pi \int_X^\infty dr r \Delta n(r) . \quad (D.8)$$

It is also easy to write $E_{\text{core}}(X)$ as a linear combination of the functions F and G . If one renames $\vec{t} = \vec{s}-\vec{X}$ and takes the Fourier transform of $\Delta n(\vec{t}+\vec{X})$, the integral over $\vec{t}$ can be calculated with the result

$$E_{\text{core}}(X) = \frac{Z}{X} \frac{2}{\pi} \int_0^{\infty} dq \Delta n(q) \frac{1}{q} \sin(qX) \{1 - \cos(qr_c)\}. \quad (\text{D.8})$$

One returns to r -space by taking the inverse Fourier transform of $\Delta n(q)$ and, after calculating the integral over q :

$$\begin{aligned} E_{\text{core}}(X) = \frac{Z}{X} 4\pi & \left[\int_0^X dr r^2 \Delta n(r) + X \int_0^{\infty} dr r \Delta n(r) - \right. \\ & - \frac{1}{2} \int_0^{X+r_c} dr r^2 \Delta n(r) - \frac{1}{2} (X+r_c) \int_{X+r_c}^{\infty} dr r \Delta n(r) - \\ & \left. - \frac{1}{2} \int_0^{X-r_c} dr r^2 \Delta n(r) - (X-r_c) \int_{X+r_c}^{\infty} dr r \Delta n(r) \right]. \quad (\text{D.9}) \end{aligned}$$

Since

$$\int_0^X dr r^2 \Delta n(r) = F(0) - F(X), \quad (\text{D.10})$$

the sum $E_{\infty}(X) + E_{\text{core}}(X)$ can be calculated, and one obtains

$$\begin{aligned} E(X) = \frac{Z}{2X} & \{F(X+r_c) + F(X-r_c) - X\{G(X+r_c) + G(X-r_c)\} - \\ & - r_c\{G(X+r_c) - G(X-r_c)\}\}. \quad (\text{D.11}) \end{aligned}$$

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Acknowledgments

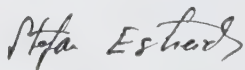
It is a pleasure to thank PD Dr. Peter F. Meier for his constant help and his far-seeing advice, for his remarkable patience and his permanent good-mood, for his wide knowledge and his well-known modesty, for his qualities as a man and as a physicist.

Acknowledgments are also due to Dr. M. Manninen for numerous constructive discussions and suggestions, and for critical reading of the manuscript. Thanks also to Prof. A.B. Denison, Prof. W. Kündig, Dr. B. Patterson, Dr. J.W. Peterssen, Dr. W. Reichart and Mr. M. Celio who were constantly ready to discuss and to help.

Thanks finally are due to Prof. A. Thellung who supervised the present work and always provided me with all possible facilities to complete it under the best conditions.

Dr. B. Patterson and Dr. R.E. Pixley accepted the job of correcting the grammar in the final text. They can be sure that I will always be ready to correct any paper they would write in French.

Zürich, October 1982

A handwritten signature in black ink, appearing to read 'Stefan Estreich', written in a cursive style.

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Oulevay, Parthe, Peter, Piron, Ronga, Ruegg, Siegfried, Spitzli,
Steinig, Thom, Vuilleumier, Walker, Weber, Zinn.
- Universität Zürich: Meier, Rasche, Thellung.

